FUNDAMENTAL ASPECTS OF THE DEHYDRATION OF FOODSTUFFS

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SESSION I

Chairman: Dr. J. R. Nicholls

PLANT STRUCTURE AND DEHYDRATION

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The production of dried fruits is an old- and well-established industry in several countries: the following table shows total production figures for 1955.

Production of dried fruits in 1955
(thousand tons)

	Prunes	Figs	Apricots	Peaches	Apples	Pears	Currants and raisins	Dates
Algeria		21·0						
Argentina	6·1			1·6		0·6	6·5	
Australia	2·3		1·6	0·7	1·0	0·1	79·5	
Canada					0·8			
Chile	4·0			0·9				
Cyprus							7·0	
France	7·0							
Greece		25·2					102·4	
Iran			5·4				54·5	
Italy		38·5					1·6	
New Zealand					0·2			
Portugal		9·0						
South Africa	3·0		0·8	1·7	0·1	0·2	9·2	
Spain			0·8				12·5	
Turkey		28·0					39·0	
United States	121·3	22·6	12·9	6·3	10·6	3·4	200·0	
Yugoslavia	22·3							
Total	166·0	144·3	21·5	11·2	12·7	4·3	512·2	480*
Drying ratio	1·5:1	4:1	5·8:1	4·8:1	8·3:1	5:1	3·6:1	1·2:1*
Equivalent fresh product	249	576	124	54	105	21	1846	576

*Approximate estimate.

Onions, herbs and chicory, being important as flavourings, are available in a dehydrated state and take their place alongside the traditional sun-dried spices. In the dried state most of these can be regarded as derived or new products, in that they are not required to reconstitute to an original pre-dried state. Apples, apricots, pears and peaches are the exceptions. In comparison with these large figures the production of the 'modern dehydrated' fruits and vegetables is very small. Dehydrated apple tissue, which is a by-product of the fresh fruit trade, represents only a very small fraction of the world crop and the other dehydrated fruits are by-products or ancillary to fresh or canned forms.

When a dried product has to be reconstituted to a state as similar as possible to the freshly cooked product and has as competitor canned or quick-frozen material, as with carrot and potato, the problems of dehydration change. Means of accurate comparison with the fresh material are then required, and subjective assessment in terms of colour, flavour and texture are usually used, as well as chemical analysis for nutrients and vitamins. In general, it is found that material which is acceptable by subjective tests is nutritionally adequate, in fact, the estimation of the content of ascorbic acid can be used as a sensitive index of quality and hence of the method of processing.

Structure of a typical plant cell and of plant tissues

Living cells have an active metabolism and one index of this is their respiration, usually oxidation of simple sugars to carbon dioxide and water, which produces the energy to maintain their organization. A typical unspecialized cell is approximately 1×10^{-3} cm. in diameter and has a cellulose wall making it a 12- to 14-sided polyhedron. Between adjacent cells is the middle lamella, composed of pectic compounds, which serves to cement the cells together and which under certain conditions may soften and allow the cells to separate.

In living cells there is a layer of protoplasm immediately inside the cell wall in which is embedded the cell organs, such as the nucleus, plastids, mitochondria as well as granules of reserve materials such as starch, protein and oil. Protoplasm is a fairly fluid protein solution and the enzymes, which are jointly responsible for all cell activities, are in it or in the protoplasmic inclusions.

The inner boundary of the protoplasmic layer is a relatively tough semi-permeable membrane and inside it is the vacuole, an aqueous solution of many compounds. This semi-permeable membrane is responsible for the cell acting as an osmotic system.

Thus a plant cell consists of a minute droplet of solution surrounded by an osmotic membrane and enveloped by a strong case, the cell wall, with free water on the outside. The osmotic suction sets up an internal hydrostatic pressure, called the turgor pressure, which is balanced by the inward pressure of the cell wall. It is this turgor pressure, acting in each cell, which is responsible for the firmness of non-woody vegetable tissue and the desirable crispness of raw vegetables and fruits.

The unspecialized cell described may be modified by protoplasmic inclusions, by marked change of shape, or by alteration of the cell wall. The protoplasm, for instance, may contain a large number of reserve food granules, such as starch in the potato, starch and protein in pulses, and oil droplets in certain seeds, and the amount of soluble material varies widely, sucrose may be as high as 20% or so low as to be barely detectable.

The cell wall may be strengthened by inter-penetration and incrustation with lignin (linked phenolic residues) or it may be overlaid by massive deposits of cellulose with the formation of tissues which in their most developed state are hard and woody but at lower levels of lignification are merely tough. Lignified cells are usually greatly elongated and normally comprise the fibrous part of vegetables and when mature are dead, being devoid of protoplasm.

Each cell when young is joined to its neighbours on all sides but during growth small splits occur in the middle lamella of the cell wall and lead to the production of minute air spaces between the cells. These, characteristically, occur at the corners of the cells and form a continuous system of air channels for ventilation of the tissue.

The effect of cooking on tissue

The organization of a living cell can be easily disturbed by mechanical injury, poisons, freezing, etc., when the tissue loses its turgor and becomes flaccid and quite rapidly uncontrolled chemical changes (autolysis) occur, the more obvious ones being alterations in colour and odour. Heating leads to rather different changes in tissues. It coagulates the bulk of the protoplasmic proteins and so destroys the enzymes which produce the autolytic changes that normally occur on the death of a cell. It also destroys the membrane surrounding the vacuole and with it the osmotic properties of the cell. The wall shrinks inwards when the turgor is released and liquid is forced out into the intercellular spaces and in some cases right out of the tissue. The natural crispness of the tissue goes. If starch is present it is dispersed and the starch gel comes to occupy the greater part of the cell setting up a certain imbibitional force. It is worth noting that the water in a cooked potato is held in an essentially different manner from that in a cooked carrot or cabbage as in the former case water cannot be expressed by low mechanical pressures whereas in non-starchy vegetables a few g. per sq. cm. is sufficient pressure to express some of it.

After the death of the cells by heating in water, the continued immersion in the cooking liquor enable solutes to leach out of the cells and losses may be very high. Conversely, penetration of solutes foreign to the cell and which would penetrate very slowly into undamaged tissue can now enter more rapidly, e.g., sulphur dioxide or sulphite ions and alkali or acid, so that some control of the chemical environment of the cooked tissue becomes possible. For exact control to be exercised at various stages of processing as in blanching, tray loading and drying, the vegetables must be cut into small pieces of uniform size. Rates of drying as affected by shape, tray loading, temperature, humidity, rate and type of air movement are the subject of a later paper (see Ede, p. 136) and will not be dealt with here.

Pre-drying treatment

Raw dried vegetables after cooking do not approximate closely to the freshly cooked product and a pre-drying heat treatment is usually carried out. This consists of scalding the tissue, i.e. maintaining it above a certain minimum temperature for a definite time, and this seems

(1) to allow the tissue to soften when cooked after drying—tissue dried raw will not always soften at this stage;

(2) to prevent off flavours and colour resulting from autolytic reactions;

(3) to introduce compounds into the tissue and thus partially to control its chemical environment;

(4) to sterilize the tissue.

Although scalding is usually regarded as essential, it has some undesirable effects in that it makes drying more difficult because of ' water logging ' of the tissues, losses of soluble nutrients may be considerable, especially when scalded in water and, unless carefully controlled, potato and cabbage may become over-cooked and disintegrate by softening of the middle lamella.

As there is no alternative yet available to a pre-drying heat treatment, a number of alternative methods have been considered. Thus in serial water scalding the same liquid is used repeatedly, so as to build up and maintain a concentration of solutes in the liquor and thereby prevent losses from the tissue. Unfortunately the prolonged heating is liable to induce undesirable changes in the solutes and their entry into the tissues may lead to a reduction in the storage life of the dry product.

Scalding in steam does not cause leaching to the same extent as water-scalding but chemical treatment is more difficult. Scalding without leaching can also be affected by treatment with hot air saturated with water vapour or by scalding partially wilted material or by dielectric heating, but all methods have their individual difficulties and advantages.

The properties of the scalded tissue in relation to drying

The nature of scalded tissue raises problems and imposes limitation on the process of drying which are considered below.

(1) Reactions may occur during drying which lead to ' browning ' of the tissue (see later paper by Lea, p. 178). These reactions, which usually involve amino-nitrogen and other constituents such as simple sugars or organic acids, are slow at high and very low water contents and have a high temperature coefficient. Thus the temperature of the drying material must be kept low, especially at intermediate water contents. Furthermore, during drying, colourless precursors of the browning reactions may be produced which will reduce the storage life of the dried product. It follows from these considerations that, at all stages, holding at a high temperature is undesirable and any process that involves double drying of material should be avoided if possible, e.g., some of the techniques for compression of non-thermoplastic dried vegetable, etc.

(2) Waterlogging of the air spaces affects the rate of loss of water from the inner zones and the tissue must therefore be cut into relatively small pieces for drying to be completed within a reasonable time. Drying *in vacuo* partially overcomes this difficulty but introduces others, such as transfer of heat.

(3) A major unsolved problem is the loss of volatile flavouring constituents which occurs with all tissues but is much more marked with the more aromatic vegetables such as carrot or celery than in potato or cabbage.

(4) Starchy vegetables, such as potato, dry to a more or less continuous starch paste and sugary vegetables, such as carrot or cabbage, dry to a continuous sugar syrup supported on a cellulose framework. In both cases the nearly dry tissue is devoid of pores, so that diffusion of water through the mass is greatly retarded in comparison with raw or vacuum-dried tissue which is porous.

(5) Changes in the physical properties of the cell wall must be avoided. When a dried vegetable is put into water the walls absorb water and soften and then, owing to their natural elasticity, tend to return to their original shape and in so doing suck water into the cavity of the cell. In starchy vegetables there is also the imbibitional force of the starch gel assisting water uptake. Both the elasticity of the cell wall and the swelling power of the starch gel are reduced by heat treatment, whether during drying or storage at elevated temperatures.

(6) Undue heating during the early stages of drying must be avoided as over-cooking would result, leading to disintegration on reconstitution.

(7) The drying temperature must not be so low as to allow of the growth of bacteria, thermophilic or otherwise.

(8) Pressure on the scalded vegetables must be avoided since it leads to loss of juice as drip.

The properties of cabbage, carrot and potato in relation to drying

Cabbage

The green water-insoluble pigments of plants, the chlorophylls, are always localized in plastids in the cells and when they are absent, as in the inner leaves of cabbage, there is usually present more or less carotenoid material to give the tissue a white to yellow colour. During scalding, control of the pH at about 7·0 is necessary to retain a good green colour, scalding under slightly acid conditions producing a dull olive green and alkaline conditions a rather vivid blue green.

The flavour constituents of raw cabbage and of cabbage dried raw are easily decomposed whereby a very offensive odour is produced: this is prevented by adequate scalding.

Fresh cabbage may be readily over-cooked to give a mush while at the other extreme raw dried cabbage cannot be softened even by cooking. Scalded and dried cabbage when cooked is tougher than freshly cooked but has the advantage that it cannot be over-cooked to a mush.

Carrot

The colour is due to insoluble carotenoids which are stable during the normal process of scalding and drying. Some stocks of carrot contain a tannin which reacts with iron derived either from the tissue or the scalding liquor to give a blue black discoloration. This can be avoided by scalding in a weak solution of phosphate at a sufficiently alkaline pH to precipitate the iron.

In dried carrot the main flavour tends to be sweetness and the characteristic odour of fresh carrot, due to a volatile oil, is mainly lost during drying.

Fresh carrot tissue does not disintegrate on excessive cooking and only some stocks of carrot when dried raw are tough. In other cases scalding has little effect on the texture of the dehydrated and cooked product.

Potato

Oxidative enzymic reactions occur in damaged potato tissue which result in the production of dark melanoid pigments and these can also be formed during drying if scalding is inadequate. Another type of discoloration arises from the presence of polyphenols in the tissue which react with iron, derived from either the potato tissue, the water, the scalder, the drying trays, etc., to give a bluish colour, which in the fresh cooked tuber is called ' stem-end blackening '. This may be controlled via the pH of the tissue and iron contamination should be avoided.

Potato dried raw usually has a rather ' brittle ' texture, but a very short scald gives a satisfactory material. It is desirable to have as few broken cells as possible in the dried material thereby avoiding the escape of the starch gel which gives to the reconstituted product an unpleasantly sticky texture. Potato starch gel does not rehydrate well, as is known to the manufacturers of rapid-reconstitution soup powders. Long storage of the dried potato, especially at high temperatures, leads to a further decrease in rehydration power with the development of a dry and mealy product.

The dried product

The dried vegetables, containing some 3–6% of water and in equilibrium with 10–30% relative humidity, are unstable and hygroscopic. During storage a loss of flavour occurs together with a slow increase in toughness and decrease in rehydration, there may be a development of brown compounds (see below, Lea, p. 178) with a ' burnt ' off flavour, or a rancid type of off-flavour may develop and carotene may be oxidized. These changes are decreased by storage at a low water content and at a low temperature except that rancidity increases at low water content. Addition of sulphite reduces the browning reactions both during drying and storage, and rancidity and carotene oxidation are virtually stopped by storage in the absence of oxygen. As might be expected, except for the browning reaction, these deteriorations are shown to very different degrees by different vegetables, the mild flavoured potato shows rancidity, while carotene oxidation is serious in carrots although potato also bleaches due to this cause. The handling of all dried products, therefore, requires great care.

In a general way it may be said that the various deteriorations that occur during drying continue during storage at a rate controlled by the moisture content and temperature. This

continuity of the deterioration reactions emphasizes the necessity for the exact limitation of the drying process as otherwise quality and storage life will be affected.

The ideal nutritive requirement of a dried vegetable is that it shall contain all the materials present in the raw vegetables in an unchanged state. An approach to this condition involves low leaching losses during scalding, low levels of chemical change during drying and a small loss of volatile materials, other than water, at any stage. Unfortunately low leaching losses are usually unfavourable to easy drying, to a good colour of the dried vegetable and to high-temperature storage. In fact, as might be expected, the more soluble constituents that are present the more labile is the product. As was said earlier, this is to some extent affected by the methods used to avoid leaching.

In any production of dried vegetables a balance has to be made between the practical problems of scalding and drying on the one hand and the ideal nutritive requirement, the storage life and subjective judgment of quality of the dried product on the other. In fact, in the drying of vegetables to make an acceptable food none of these problems can be considered in isolation.

Acknowledgment

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Discussion

Mr. E. G. B. Gooding: (1) Dr. Gane has suggested that waterlogging of the tissue resulting from scalding makes drying more difficult. We have a large number of figures for potato, cabbage and carrot. In our standard drying period of 6 hours, only in the case of carrot does the unscalded vegetable come to a lower final moisture content than the scalded. Of course, without curves following the whole course of drying for the two types of material one cannot say that scalding is having no effect on the rate of drying but the final practical result is nil for cabbage and potato, and only small for carrot.

(2) Does Dr. Gane have any information on the relationship between the degree to which a tissue is dehydrated and the extent to which it will subsequently reconstitute? Can he say what is the mechanism which prevents a tissue (other than potato) from recovering the full amount of water lost in dehydration? We have results from preliminary experiments with carrot which suggest that the degree of inability to reconstitute fully runs parallel with the degree of dehydration; even when the moisture content is reduced from the initial 90% to about 80%, full reconstitution could not be obtained, and with lower moisture contents the percentage reconstitution (i.e., $\frac{\text{reconstituted weight} \times 100}{\text{original weight}}$) became progressively less.

Dr. Gane: (1) Mr. Gooding's comment is an interesting one in so far as it applies to the standard drying period of 6 hours and also when the final water contents are considered.

(2) I know of no work on the relationship between the water content of the dehydrated vegetable and its percentage reconstitution. Tissue does not reconstitute to the turgid fresh weight where each cell is expanded under a considerable osmotic pressure. The osmotic system is destroyed by scalding so that during reconstitution there is no osmotic activity and therefore no possibility of distention of the cells. Reconstitution in non-starchy vegetables is the result of the natural elasticity of the wet cell walls and any treatment damaging this, e.g., excessive heat during drying or long storage, reduces reconstitution.

Mr. J. F. Hearne: Dr. Gane states that, during drying, colourless precursors of the browning reactions may be produced which will reduce storage life of the dried product. Is there any direct evidence that these precursors are formed in properly produced commercial dehydrated vegetables, particularly as many are sulphited and this confers some resistance to heat damage. Also much dehydrated vegetable is bin dried for lengthy periods and as far as I can ascertain the storage life is about the same as for material dried in shorter periods.

Dr. Gane: Presumed precursors of the browning reaction are present in normal commercially dried carrot, cabbage and potato whether dried with sulphur dioxide or not. Sulphur dioxide does not appear to stop the formation of precursors of the browning reaction; it only stops the formation of the coloured compounds.

THE STRUCTURE OF THE ANIMAL TISSUES AND DEHYDRATION

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Introduction

The object of this paper is to discuss the part played by structure in the drying of animal tissues. Ideally, a dried food after reconstitution should be indistinguishable from the original material, but in practice this ideal is only likely to be approached with a liquid such as milk. It is unlikely, for example, that it will ever be practicable to dry, to store and to reconstitute successfully an intact egg or a quarter of beef, and to that extent, therefore, the drying of meat or eggs will probably always involve some preliminary loss of structure. This obvious limitation has not been a bar to the development and use of various forms of dried eggs and dried meat, but it has meant that the most successful forms are those which meet a specific and limited need. The limitation also suggests that for the purpose of this paper the word 'structure' should be interpreted liberally since often it is not so much the original physical structure, as such, that is important as some functional property of the material that depends ultimately on its molecular or fine structure. These points can perhaps be illustrated by considering a dried food that has been an important article of commerce for many years; namely, dried egg albumen.

Dried egg albumen is more useful to the sugar confectioner than fresh egg white because of its stability and because it can be dissolved to give solutions of any desired concentration. It is no disadvantage to its users that during its manufacture the complicated physical structure of the parent egg white has been destroyed so long as the property of forming stable, heat-coagulable foams has been retained. In fact, the destruction of the mucin gel which makes up about one-half the volume of fresh egg white is an advantage, since otherwise energy must be expended in destroying it during beating. Equally relevant in the present context is the fact, empirically discovered in China, that egg white dried without any preliminary treatment does not retain its foaming properties unchanged during storage, whereas it does so if it is submitted to bacterial fermentation before drying. The reasons for this are now known and dried egg albumen prepared in this manner has become the classical example of the prevention of a glucose–protein reaction in a dried food. It is also an example of the way in which the need to preserve some essential function of the product has complicated the simple removal of water. It is this mutual relation between structure or function, on the one hand, and methods of production on the other that is discussed here.

Another property of a dried food that is related to its structure is the ease with which it can be reconstituted. This property is not merely a matter of convenience for the user. If the product reconstitutes slowly, or slowly without stirring, it may sometimes be soaked in water at ordinary temperatures for unduly long periods, and if, as is often the case, the dried food is not sterile, an undesirable degree of bacterial multiplication may occur. The position is rendered more serious when, as with egg products, the sample may occasionally contain members of the *Salmonella* group capable of causing food poisoning. The numbers present in dried eggs are normally too small to present a hazard, but danger can arise under the circumstances outlined above if the reconstituted material is eaten without adequate cooking. Because of this risk, liquid whole egg and liquid yolk are often pasteurized before drying. It is difficult to pasteurize liquid egg white effectively without impairing its foaming properties, but it is possible to destroy salmonellas in dried crystal albumen by heating it, and this process is now being applied in this country to the imported product.[1] It will be seen that this is another example of the tendency of dehydration to accumulate ancillary processes around itself.

Dried egg

Spray-dried whole egg (an intimate mixture of the white and yolk) was manufactured in large quantities during the second world war; the average yearly import into the United Kingdom during 1942–45 was 61,000 tons. It served as a substitute for the shell eggs normally used by the housewife and the frozen egg normally used by the baker, but in neither case was the substitution a complete success. Transport difficulties and the accumulation of buffer stocks so lengthened the period between manufacture and consumption that flavour deterioration

was often evident in scrambled eggs and omelettes. The baker, on the other hand, was more concerned with the marked loss of foaming or aerating power that accompanied spray-drying. Even when freshly prepared under the best conditions, the foam volume after reconstitution and beating was roughly halved, and the product was unsuitable for the making of cakes that depended upon the egg for aeration. Moreover, there was a further loss during storage as the solubility of the powder decreased.

Flavour and solubility changes during storage could be retarded by lowering the water content from the normal 4–5% to 2%. This was done[2-4] in the United States without impairing the quality of the product or lowering its rate of production by the ingenious device of pre-heating the liquid to 140°F immediately before it entered the spray-dryer, thereby increasing the degree of atomization. Lowering the pH of the liquid before drying by the addition of acid also helped, but no great increase in stability as regards flavour or solubility over the war-time product was achieved until it was found that changes in these properties during storage were caused by the reaction of glucose with the amino groups of proteins and kephalin, and that these reactions could be prevented by destroying glucose before drying by fermentation with either yeast or glucose oxidase (notatin).[5–11]

Liquid whole egg does not yield such copious foams as egg white when beaten, presumably because the unfolded, linked molecules of globular proteins which stabilize egg-white foams so efficiently have been replaced at the air–liquid interface by a mixed lipid–protein layer that is less efficient. It is possible, in fact, to demonstrate a progressive decrease in the elasto-viscosity of the surface layers of egg white as increasing amounts of yolk are mixed with the white.[12] We are concerned here, however, with a marked loss of foaming power caused by the spray-drying of liquid whole egg, a change that does *not* occur when egg white is either tray- or spray-dried. The change is not the result of protein denaturation during spray-drying since, as far as can be judged from solubility determinations, this does not occur to any significant extent when the drying conditions are properly adjusted; nor does the removal of glucose from liquid whole egg prevent the loss during drying although it prevents further loss during storage.[6] There is evidence, however, that spray-drying liberates some component from the yolk constituents of a lipid nature that inhibits foaming; thus, the addition of reconstituted spray-dried whole egg to fresh liquid whole egg reduces the foam volume to a considerably greater extent than the addition of an equal volume of water.[13,14]

The freeze-drying of liquid whole egg also reduces the foaming power but the reduction is never so great as with spray-drying. The greater loss in the latter case may be due to the moderate degree of heating experienced during spray-drying (although the temperature of the particles seldom exceeds 40–50°C), but it is possible that the shear forces experienced during atomization may also play a part in the partial breakdown of the fat and phospholipin–protein complexes contributed to whole egg by the yolk.

It was found that the loss of foaming and baking properties could be prevented if 10–15% of sucrose or lactose were dissolved in liquid whole egg before spray-drying, and that there was little subsequent loss during storage.[15] Large amounts of dried sugar–egg, using sucrose, were manufactured in Canada and Australia. The powder is extremely stable so long as the water content does not exceed 3·5%.[16,17] An interesting finding[18] with pressure-jet spray-dryers was that the smaller the nozzle aperture, and hence the smaller the average particle size, the better were the baking properties of the powder. It seems probable that the basis of this relation is that the rate of drying of the atomized particles has an effect on their baking properties, since a decrease in nozzle diameter increases this rate without the need for raising the inlet and outlet air temperatures of the dryer unduly (which has an adverse effect). If this were so, pre-heating of the sugar-egg mixture to 140°F before spray-drying should also improve the baking quality of the powder, which was found to be the case.[18]

No explanation of the protective action of sucrose can be offered, although there is evidence[13] from experiments on the extraction of fat and phospholipins with different solvents that there is a difference in the state of the lipids in ordinary spray-dried whole egg, on the one hand, and fresh whole egg and egg dried with sucrose on the other. Presumably, therefore, sucrose prevents the partial breakdown of lipid complexes, but it is not clear how it does so. The presence of sucrose also retards the loss of solubility during storage, but there seems to be no connexion between the mechanism of the two protective effects since the preservation of solubility

apparently depends on the inhibition by sucrose of the complex series of reactions which follow the preliminary condensation of glucose with amino groups.[19]

Less is known about dried yolk. Neither fresh nor dried yolks yield copious foams when beaten, and the uses to which they are put depend upon their emulsifying properties and those properties described as binding, moistening and shortening which are more easy to recognize than to define and measure. It is known that the stability of dried yolk during storage is improved by the removal of glucose before drying.[19,19a] Drying undoubtedly produces changes in structure which seem to be analogous to the changes commonly known as gelation which occur when yolk and, to a much lesser extent, when whole egg is frozen (for example, dried yolk after reconstitution has a pasty consistency), but these changes seem to have no adverse effect on the usefulness of the product.

Dried eggs do not reconstitute very readily but not because some of them have a high lipid content; dried albumen, whether tray- or spray-dried, is not very much better in this respect than spray-dried whole egg. Unless the mixture is stirred and worked, clumps of unwetted powder tend to become coated with a swollen, gelatinous layer through which water penetrates slowly. Instead of stirring, therefore, the mixture is often left sometimes for excessively long periods. It is interesting that spray-dried whole egg which has been overheated during drying and which consequently has a lowered solubility, is wetted by water more easily than a sample of good quality. In extreme cases, poor samples ' cream ' almost completely after reconstitution because the original structure of the spray-dried particles (which are in the form of armour-plated bubbles) is not destroyed by wetting.

Although many of the original defects caused by the drying of eggs have been remedied, there has been no real change in the general preference for shell eggs and frozen eggs as opposed to dried eggs (apart from dried albumen which has always occuped a special position in sugar confectionery). Large amounts of dried eggs (spray- or tray-dried albumen, spray-dried whole egg, spray-dried sugar–egg and spray-dried yolk) are manufactured—to the extent of roughly 9000 tons per annum in the United States, for example—but this is mainly because they are used in the preparation of dried cake mixtures, the sale of which has increased steadily in recent years.

Dried meat

Large amounts of dried meat were manufactured during the war; the preparation and properties of the products have been reviewed by Sharp.[20] In the process developed at the Low Temperature Research Station, the meat after trimming was sliced and lightly cooked, minced coarsely and dried as a thin layer in an air-stream at 70–80°C. Extractives were added back to the minced meat before drying in the form of the vacuum-concentrated, cooking liquor. After reconstitution, the product was very similar to, and could be put to the same uses as, the undried, cooked minced meat, the chief difference between the two materials being the slightly inferior texture of the dried product.

Although mincing before drying by-passed many of the problems associated with the drying and eating of large pieces of meat, the texture and juiciness of the particles were still important, and were adversely affected by unsatisfactory conditions of pre-cooking, drying and storage.[20] Texture and juiciness were found to be associated with the amount of water absorbed by the dried meat on soaking. Expressed as a percentage of the raw meat equivalent, the re-absorption value after 24 hours' soaking for samples of good quality ranged from 85–90; samples of inferior texture gave lower values. Absorption was rapid, most of the water being taken up in less than 2 hours.[20,21] Considerable attention has since been paid to water absorption as an index of quality.[22–25]

Much recent work has been devoted to the drying of larger pieces of uncooked meat such as steaks and chops in which the grosser physical structure is retained. The chief methods used for this purpose have been freeze-drying and the vacuum contact plate process[26–28] which is being examined at the Research Establishment of the Ministry of Agriculture, Fisheries and Food at Aberdeen. Generally speaking, pre-freezing of the meat is considered to be desirable in both processes. Reviews on freeze-drying have been published by Flosdorf,[29] Gane[30] and Harper & Tappel.[25]

Although freeze-drying might be expected to produce the minimum of change, it appears from recent work that freeze-dried meat has a drier and tougher texture than the frozen

control.[25] This finding agrees with the results of early experiments on the freeze-drying of raw steaks carried out at the Low Temperature Research Station. The dried steaks absorbed about 90% of the water they originally contained, but on grilling they lost considerably more water than the control, and their texture was tougher and drier. Deficiencies in texture have been attributed to the loss of water-holding capacity by the muscle proteins, and protein denaturation during drying has been suggested as the cause of this loss. It is of interest to discuss these suggestions in some detail since changes in texture are said to be the principal problem associated with the freeze-drying of meat.

Although denatured proteins are less hydrophilic than the original native proteins, denaturation, as such, need not lead to a loss of water-holding capacity;[31,32] for example, some proteins such as egg albumin are incapable of forming gels in the native state but are able to do so in the denatured state. It is necessary, therefore, to define more closely what is meant by water-holding capacity. The amount of water bound to proteins so firmly that it is either unable to act as solvent or is able to contribute to the rigidity or elasticity of the system is small. Work on the vapour pressure isotherm of the sartorious muscle of the frog[33] indicated that the bound water unable to act as solvent was only about 0·3 g. of water per g. of protein, and that the value for beef muscle was about the same.[34] The most probable value of the amount of water immobilized by solvation by a number of proteins has been estimated to be considerably less than 0·5 g. of water per g. of protein.[35] The ability of muscle to hold water would seem to reside, therefore, in the possession of a system of membranes and of structural proteins which are capable of forming gels by enclosing water in a three-dimensional network of threadlike protein chains. It is known that the ability of such cross-linked networks to hold liquid or to absorb it again after drying does not necessarily imply any attractive forces between the network and the solvent.[36]

It is clear that dried meat which will only absorb a fraction of the water it formerly contained has been damaged by drying but almost complete absorption does not mean that the meat has regained its former structure. It must be remembered that fresh raw meat will also absorb water on soaking, and that if no solutes were leached out it would continue to do so until the elastic reaction of the stretched membranes balanced the osmotic pressure within them. The water content of the sartorious muscle of the frog dried to constant weight in air of successively lower relative humidities down to complete dryness over P_2O_5 was found to be regained when the reverse process was carried out up to a relative humidity of 96%.[33] Unfortunately, the uptake curve could not be followed further since at 99·4% R.H. (the equilibrium vapour pressure of fresh frog muscle in rigor) the rate of water uptake was so slow that mould growth occurred before equilibrium was reached. Nevertheless, practically complete reversibility would be expected, since under these conditions the water content at high humidities is mainly governed by the amount of solutes in the muscle (equivalent with fresh frog muscle in rigor to 0·2M-NaCl), and not by the small amount of water firmly bound to proteins. In any case, there is no opportunity under these conditions for solutes to leach out. For the same reasons, reversibility in water vapour is not an indication that the structure of the protein framework has not been changed by drying.

Presumably, the reconstitution of dried meat by soaking is complicated by the leaching out of solutes, since the consequent changes in ionic strength might also be expected to influence the expansion of the protein framework. It is possible that some information might be gained about the way water is imbibed and held by comparing the amounts of water pressed out of reconstituted dried meat and fresh meat by a series of increasing pressures as was done by Jordan Lloyd & Moran[37] in the case of gelatin gels.

Sartorius muscles dried at 104 c were found to be almost incapable of absorbing water into their structure when exposed to air of high relative humidities. Instead, after a small initial absorption, water condensed on the surface of the muscle, and after extracting some solutes, dripped away slowly in a succession of drops. It seems reasonable to assume that heating introduced so many extra cross-linkages in the protein chains that the structure became rigid in much the same way as rubber becomes almost incapable of swelling in an organic solvent if too many cross-links are introduced during vulcanization. It is tempting to assume that similar changes, although much less pronounced, might be responsible for deficiencies in the texture of dried meat. That meat dried by heating should suffer such changes seems to be reasonable

but it is not easy to envisage them occurring during freeze-drying. Nevertheless, dried meat, like dried eggs, is subject to non-enzymic browning reactions.[38–43] It is conceivable, therefore, that networks might be cross-linked during drying by primary chemical bonds resulting from these reactions, and that changes in texture during storage might be the result of further cross-linking. Connell [44, 45] has suggested that the chief cause of the toughening of fish muscle on drying is the tendency of the proteins to form cross-linkages.

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Discussion

Mr. M. Spencer (National College of Food Technology, London): With regard to the analogy, suggested by a speaker in the discussion, between the loss of aerating power of spray-dried eggs in cakes, and the property of dried milk to depress leaf volume; this latter effect is produced by both spray- and roller-dried milk, and the effect is an entirely different one as it effects the quality of the gluten by another mechanism.

Dr. Brooks has said that the disruptive forces acting on the egg during spray-drying decreased the foam-forming properties in baking. Is there evidence that other methods of drying do not produce this effect? Could Dr. Brooks explain further the mechanism involved by which these disruptive forces produce these changes (in the lipo-protein of egg)?

Dr. Brooks: I would not go beyond saying that the shear forces exerted during the spray-drying of liquid whole egg might be partly responsible for the inferior foaming power of dried whole egg. There seems to be no direct evidence, but the loss of foaming power is markedly smaller when whole egg is freeze-dried. Furthermore, American work has shown that if large shear forces are exerted during the homogenization of liquid egg albumen, its foaming power is greatly impaired,[1] and also that it is readily damaged by atomization during spray-drying.[2] As far is I know, the precise mechanism is unknown.

Dr. C. H. Lea: Dr. Brooks's suggestion that the loss of aerating power which occurs when whole egg is spray-dried may be due to the liberation of some lipid, is an interesting one. Presumably the lipid penetrates and weakens the protein films which stabilize the foam globules. Such an explanation seems reasonable in view of the fact that most of the lipid in the fresh yolk appears to be bound in some degree to protein and that lipoproteins of high lipid content such as the β-lipoprotein of blood plasma are not completely stable to dehydration, even by freeze-drying. We have found that lipovitellin isolated from egg yolk is considerably protected by sucrose from loss of solubility and from the splitting off of its lipid which occurs to some extent during drying and during storage under unfavourable conditions in the ' dry ' state.

This property of sucrose in protecting against loss of aerating power is a useful one although, unfortunately, some samples of sugar-dried egg have been found to be rather susceptible to another form of spoilage, namely ' fishy ' off-flavours probably arising from oxidation of the lipids.

We also found that sucrose protects the proteins of milk against loss of solubility induced by reaction with glucose in the ' dry ' state, but it had no effect on the rate of the primary combination of the protein amino groups with the reducing sugar, nor did it inhibit the discoloration which subsequently occurred when the protein–sugar mixture was stored.

Dr. Brooks: We noticed after the first plant-scale trials early in 1944, that sugar-dried egg tended to develop a fishy odour when kept in air. Although this defect seemed to have little importance when it came to making cakes, we did test the effect of gas-packing but on this occasion neither the control nor the gas-packed powder became fishy. This proved to be characteristic; fishiness sometimes appeared on storage in air and sometimes did not, without any apparent reason for the difference. There is no doubt that the material is more sensitive to oxidation than ordinary dried whole egg, but the difference between batches suggests differences between low levels of metallic catalysts, possibly accidentally acquired.

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' BOUND WATER ' IN FOODS

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The role of water in food is described and also the forms in which it may be ' bound.' The possible effects of decreasing water content and the problem of the reversibility of changes are discussed, and some examples are given of biochemical, biological and technological reversibilities where an optimum water content gives maximum reversibility. Total water content cannot be separated into ' free ' and ' bound ' water and an explanation is given for this.

The freezing method is suggested as the most accurate procedure for determining ' unfreezable ' water, especially when this is related to the protein content of the food and not to its total solids. A summary of recent work is given showing that in protein foods there is an almost stoicheiometric relationship between ' unfreezable ' water content and protein nitrogen of two molecules of water to one atom of protein nitrogen.

Introduction

The problem of ' bound water ' in foods has occupied many scientists, especially during the last 40 years. In studying the important role of water in different water-containing materials and its influence on their mechanical, physical, chemical and enzymic behaviour, it has been found necessary to distinguish between different forms of water-binding to hydrophilic macromolecules and at first it seemed adequate to consider the total water content as being divided into ' free ' and ' bound ' water. The conception of ' bound water ' became of special importance in all processes, where the bulk of the water is evaporated by freezing the water out, by evaporation or dehydration, or even by binding chemically. Some irreversible changes will occur in the products, when the ' bound water ' is partially removed. Since the general trend in the dehydration of foods is towards very low moisture contents, it is of importance to know more concerning the changes that occur at such low moisture contents, so as to avoid damage to the dehydrated products during processing and storage.

The role of water

Water, comprising 60–95% of the total weight of foods, is by far the dominant and the most important component of common foods, which may also contain fats and oils, proteins, carbohydrates, acids, minerals and other groups of substances. Many of these (like sugars, acids, many salts, etc.) occur in solution in the water, but others are distributed less uniformly or dispersed in these solutions. On the other hand, many substances found in the foods absorb water in different ways, and the presence of salts, like sodium chloride, citrates or phosphates, increases the water-binding power of such substances as proteins, e.g., in the swelling of minced meat during the processing of sausages. Therefore, as far as we know, free water does not exist in the foods; it is always combined in some way with other components present.

The state of water and its distribution in the biological system is of prime importance and it is obvious that changes in water content or water distribution will lead to vital changes in the product.

Possible forms of water binding

The role of water in food depends very much on the chemical composition and physical structure of the food and also on the form in which the water is present; in this respect there are the following possibilities:

(1) The water could be found in a pure form as *surface water*; in which case it is not part of the product itself, but comes from outside (condensation, washing, etc.). Such water could be considered as free water only so long as it has not mixed or reacted in any way with the surface components.

(2) The water could be *chemically* bound to some salts, etc., either by its prime valence (e.g., NaOH) or as hydrate (e.g., $CoCl_2,6H_2O$). This chemically bound water is not expelled by common methods of food processing.

(3) The water could be *adsorbed* as a very thin, mono- or polymolecular layer on the internal or external surfaces of the product by molecular forces or in fine pores by capillary condensation.

(4) The water could be adsorbed by colloid substances and remain in a gel as water of swelling due to its dipolar character; this water is also called ' water of hydration.'

It is obvious that the important forms of bound water in foods are those mentioned under (3) and (4). In addition, the water could be present as a continuous phase, in which other

substances may be dispersed molecularly, colloidally or as an emulsion; such ' solutions ' at very different concentrations could be kept by osmotic pressure within some cells, or even in some parts of cell agglomerations forming a structure, separated by semipermeable membranes.

Foods—especially those having a structure—are not at all uniform in their microscopic dimensions and there is therefore no regular distribution of water particles in them and different types of water binding will always be found in one and the same product. The different groups of substances could be distributed in water and more or less *bound* to it in the following ways:

(*a*) The water serves as medium for *molecular dispersion* of soluble substances like sodium chloride or sugar; a part of the dissolved substance can form ions. Such dispersion normally gives the most uniform distribution of the solute, provided its diffusion is not influenced by a semipermeable membrane or other means and provided the solution is not saturated.

(*b*) The water forms a *colloidal solution* by diluting hydrophilic macromolecules such as proteins, either in pure water in the case of albumins or in salt solutions in the case of globulins. Depending on the water content, two different forms of structure are possible, sol and gel, which may be changed from one form to the other reversibly. The solubility of colloids and therefore their water-binding capacity depends on pH and is minimum at the isoelectric point.

(*c*) The water forms an *emulsion* with substances of low solubility, thus giving a coarse dispersion.

The possible effects of low water content

In a given product there is an equilibrium between the different components at a given water content, independent of the form in which this water is attached to the different substances. The situation changes when water is expelled and especially when only a small amount of it remains in the food. During the expulsion of water the concentration of substances dissolved in it (salts, etc.) is increasing, possibly leading to a non-uniform distribution of water within the product. Concentrated solutions of electrolytes so produced have a very harmful effect on muscle fibres because they denature proteins. When sufficient water has been removed, the buffering action will cease and there may be a change in pH, usually a decrease because the initial value is below 7; when the isoelectric point is reached, precipitation of colloids like proteins may take place because of the effect of the pH, but the coagulation of proteins by high salt or acid concentration in the liquid phase is the main cause for denaturation, and will proceed further during storage.

The presence of water in the food is very important for properties such as structure or turgidity and even nutritive value and taste. Dehydration may affect these important properties considerably and lead to irreversible changes. The problem in dehydration is that the water content must be decreased sufficiently to improve the stability of the product by retarding the rates of deteriorative chemical, microbiological and enzymic reactions during subsequent storage; but at the same time irreversible changes should not be caused. There must also be taken into consideration the high costs of lowering the moisture content to too low a level. The residual water content of foods influences, for instance, the Maillard reaction, autoxidation of fats and oils, hydrolysis, microbial activity, etc.; but in addition the viability of seeds or even of micro-organisms may be affected by too high water content. On the other hand the resistance to high and to low temperatures depends very much on the low water content of biological material like tissues and organisms.

The analysis of the effects of a very low water content becomes difficult because some of the reactions in the dehydrated product, which might lead to irreversible changes, occur during storage and are dependent on temperature and time of storage. Experience in the storage of foods with low moisture content is that small changes of water content may influence considerably the admissible storage time. It has been pointed out that changes of this kind will be very limited when the ' free water ' content is sufficiently low or has been removed completely. This has led to industrial processes in which a part of the ' free water ' has been transformed into ' bound water ' by addition of water-binding substances (sugar, glycerol,[2] etc.), which act in some way as dehydrating agents. It is obviously clear that the ' bound water ' could be expelled or be bound in another way only if the binding forces are overcome; therefore it has been suggested[1] that that part of the water present in food which does not dissolve added sucrose is to be considered as ' bound water.'

During the storage of dehydrated products, the irreversible changes depend on the water content; at a high moisture content the changes are slower the lower is the water content; this may be explained by a reduction of the contact surfaces of the liquid phase (decreasing of reaction surfaces) and by the inhibitive effect on enzyme systems of the increasing concentration in the liquid phase. When, however, the water content passes some optimal low value (determined by a minimum of irreversible changes during the storage), other irreversible changes commence and proceed during storage of the product and are accelerated by higher storage temperature.

In some instances, irreversible changes are encouraged, e.g., paprika dehydrated at low temperature is more hygroscopic than if it is dehydrated at a higher temperature, and therefore more susceptible to moulds. Generally full reversibility of the water withdrawal from dehydrated foods is required.

From the foregoing it may be concluded that the importance of the conception of ' bound water ' is to afford an explanation of different irreversible changes in the complex system of a biological material when its water content is reduced to a very low level. It was postulated that as long as ' bound water ' remains, no irreversible reactions will occur.

Reversibility of changes

It is obvious that those substances in the food whose distribution depends on the presence of water will be most affected by removal of water. The concentration of solutes in *molecular dispersion* will increase on removal of water, until saturation is reached and they begin to crystallize. This crystallization process is normally reversible: a solution of the same concentration is obtained on addition of the same amount of water as has been expelled.

The withdrawal of water from *colloidal solution* is reversible as long as only the water used for swelling is removed; the limit of dehydration has been reached when the ' sol form ' changes into ' gel form.' It is mostly in relation to the reversibility of the water withdrawal from the colloidal substances like proteins that the term ' bound water ' is used. It is generally assumed that as long as only reversible changes are caused by withdrawal of water from proteins, the ' bound water ' or that bound to the proteins is not affected, and rehydration restores the original properties (viscosity, stability, swelling, etc.) and no visible alteration is noticeable.

Removal of water from *emulsions* leads to a breakdown of the emulsion, so much water being removed that the single emulsified particles begin to flow together and lose their dispersibility. This process must be considered as irreversible, because the former state of dispersion cannot be realized by only adding water; the breakdown into smaller particles must be done mechanically.

' Reversibility ' must be more closely defined because it seems possible to distinguish between biological, biochemical and technological reversibilities. The reversibility is the greater the more complete reconstitution of the dehydrated product is obtained after adding water. *Biological reversibility* may be of interest when the problem of the viability of organisms as influenced by withdrawal of water is involved. *Biochemical reversibility* refers to the activity of enzyme systems which may be damaged by denaturation of their colloidal substance when water is withdrawn beyond some limit. *Technological reversibility* is characterized by the complex effect of some technological processes like drying or freezing upon some important properties of products.

As an example *biological reversibility* the viability of active dry yeast may be mentioned. It is produced commercially with 8% water content and is acceptable for producing bread when stored under the conditions given in Table I.

Until recently it was known from general experience that a water content of dry yeast above 8·3% significantly shortens its shelf life[4] and that a water content below 7·5% gives a product with a greatly reduced efficiency as a leavening agent, if the dry yeast is used without special rehydration treatment. Later it was found[3] that rehydration with water vapour to a water content of about 8–10% makes possible the use of yeasts with much lower moisture content with very good results (see Tables I and II and Fig. 1). From Fig. 1 it is seen that even at the optimal water content (3–4%) some deteriorative effects take place during storage and that the optimal value remains the same independent of the time of storage. Optimum water content must not be identified with bound water content. It seems to be reasonable to assume that even if there exist such optimum water contents for other products, denaturation of proteins

Table I

Stability of commercial active dry yeast, produced in the U.S.A.,[3] packed in cans under nitrogen or vacuum, judged on acceptability of volume of loaves

Water content, %	Temperature, °C	Maximum storage time of yeast	Acceptability of bread
8	21	21 months	after 24 months not acceptable
8	32	6–9 months	—
8	49	8 days	after 12 days of storage, unacceptable
7·8	46	10 days	
5·5	46	40 days	
4·0	46	80 days	
2·2	46	170 days	
0	46	30 days	even immediately after dehydrating, only fair bread was produced

Table II

Loaf volumes of bread (ml.) made with yeasts of different moisture levels immediately after dehydration and after storage in vacuum at 46° (loaf volume = 2200 ml.: unacceptable; 2600 ml. and over: excellent) according to Mitchell & Enright[3]

Moisture level, %	Loaf volumes after storage		
	No storage	2 weeks	6 weeks
7·8	2650	1950	—
5·5	2850	(2650) — 2400*	2250
4·0	3000	(2850) — 2600*	2500
2·2	2900	(2750) — 2550*	2400
0	2350	2250	2100

Values from curves in parentheses. *Measured values.

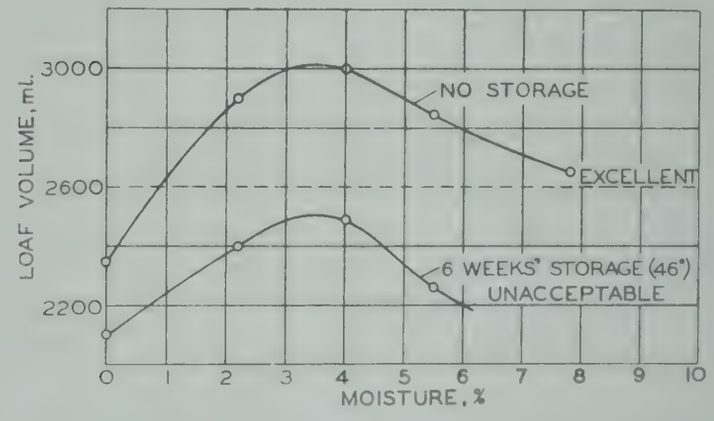

FIG. 1. *Influence of moisture content of dry yeast on loaf volume produced*

will occur during storage at optimum values in them too. At very low moisture content, a better product results with longer periods of rehydration.

There are several explanations of the mechanism of irreversible changes by too low water content. The most probable seems to be this: with cellulose it has been shown[5] that in its original water-soaked condition the free hydroxyl groups of cellulose molecules—having a secondary valence - are practically all satisfied by water; when the cellulose is dehydrated, these OH-groups lose their water and their valence could be satisfied after shrinkage by drawing adjacent cellulose molecules together. Such pairs of OH-groups may remain in this combination also during rehydration causing an irreversible change in the cell structure in this case.

A similar phenomenon has been studied recently on denaturation of fish proteins by freezing and even by freeze-drying[6] as a problem of *technological reversibility*. The increase in the toughness of the fibres, due to denaturation of the principal protein complex of the fibre

(actomyosin) and the loss of gel-forming ability, is explained as an increase in the number of cross-linkages causing larger aggregations in the protein than existed before dehydration.

It is well known that a dehydrated product never regains its original properties because it does not absorb as much water on reconstitution as was present in the original fresh material. This is especially true with protein foods like meat and fish, whose reconstitution behaviour and water-binding capacity after dehydration are not completely satisfactory. A possible explanation is given by the remarkable changes in the histological micro-structure and in the molecular structure of the fibre substance (described by Connell[6]), both of which contribute to textural and reconstitution properties of a material.[6]

The histological picture shows that the fibres lose their close contact, becoming capable of being separated easily from one another and may give—when tasted—a feeling of a fibrous, tough and dry product; besides this there are aggregations of fibres, and even areas of ' fused fibres ' separated by large spaces. The change in molecular structure of the fibres is due to denaturation of the principal protein complex of the muscle fibre (actomysin) during dehydration, accompanied by a loss of protein water gel-forming ability.

The effect of the pH value on the water-binding capacity of proteins may be mentioned here. The isoelectric point of meat muscle protein is at pH 4·5–5·0, while the meat itself at pH 5·0–5·5 has the smallest swelling and the minimum water-binding capacity. Therefore the pH value of raw meat will influence the reversibility of water removal and even the value of estimated ' bound water.' The higher the pH value of meat, the better will be its water-holding capacity.

Possible definitions of ' bound water '

From the foregoing, it is obvious that there can be no general definition of ' bound water.' As there generally is no free water in the food, the water present is always ' bound ' in some way to one or other of its components and this is a complex matter and depends on many different factors. The complex water solutions present in solid foods may not only be bound to colloid particles by hydration or as swelling liquid in gels, but also adsorbed on the intercellular surfaces and in internal capillaries; and different solutions with different concentrations could be present at different points as long as the structure of the produce is not damaged or disrupted. Because it is also obvious that the water will be bound to proteins in a manner different from that to carbohydrates or acids, it will be advisable to consider the problem of ' bound water ' with special reference to different foods or groups of foods of similar structure and composition, e.g., fish and meat. As fat does not bind water, its presence in high-protein foods can be neglected and the water present may be considered in relation to the protein alone, but it must be remembered that there may be present many different specific active groups, each having a different type of binding.

The next difficulty in the definition of ' bound water ' arises because it is based on the method used for determination. Originally the water understood to be bound was that required to form stable colloidal systems with such hydrophilic colloids as proteins or carbohydrates and a stoicheiometric relationship between water and absorbing substance was expected. Sometimes it has been suggested—as in the case of gelatin—that ' bound water ' is the water found within the micelle, and the ' free water ' in between the micelles. Later it was found that the problem is more complicated and the definition as well as the figures found depend on the method of determination used. Therefore it seems that there is no generally established and generally valid term as ' bound water.'

It is generally accepted that ' bound water ' is—by definition—that part of the water content of a product which remains in it in an unchanged (or ' bound ') state after application of the usual drying procedures, such as freezing, chemical dehydration, etc., and which can be expelled only by heating to 100–110° for a sufficiently long time. Therefore only ' free water ' can be determined by such methods as freezing, etc.

If the water which is expelled by heating at adequate temperatures—mostly at 105–110°C—is called the ' total water ' content of a product, then

' Bound water ' content = ' Total water ' content —' free water ' content.

Hence to define ' bound water ' a definition of ' free water ' content is necessary and this is given by the method of estimation as will be seen.

As a generally valid and complete description of the water-binding relationship of foods we have sorption isotherms, normally of the shape shown in Fig. 2. The ' bound water ' must appear on the curve and the point on the isotherm will be determined by a more or less arbitrarily selected method of measurement. These points could be fixed only by such methods, because only water absorbed with energy smaller than the energy applied during the measurement will be liberated and determined as ' free water '; water absorbed with a greater energy than corresponding to that point will be called ' bound.' Therefore the term ' bound water ' is a relative one. There must be a definite discontinuity in the isotherm—like that in Fig. 3—if both kinds of water binding are present. This means that the section A of the isotherm in Fig. 3 refers to the water content ' bound ' to the macromolecules and that ' free ' water will be found at the beginning of section B. Actually such a discontinuity does not exist in practice and there is always continuous overlapping of different kinds of binding. Therefore there will be found in Fig. 2 for both isotherms represented, in section A monomolecular adsorption of water on internal and external colloidal micelle surfaces, accompanied by interaction between water and absorbing substances; chemically bound water as in $Ca(OH)_2$ or $CoCl_2,6H_2O$ does not influence the isotherms of foods because at the low-temperature range studied such compounds are always stable. Because of high binding energy the sorption heat is remarkable in this section. In section B (Fig. 2) mainly polymolecular adsorption takes place; the sorption heat becomes small and the effective binding energy consists principally of latent heat of water vapour condensation. In section C the behaviour of a colloid material is different from that of a capillary porous colloidal product: in the first case (curve 1) the water condensation occurs by further polymolecular adsorption and in some small cavities which may be present; the curve 2 has a completely different character, caused by water condensation in macro capillaries ($r > 10\mu$) with no sorption heat at all.

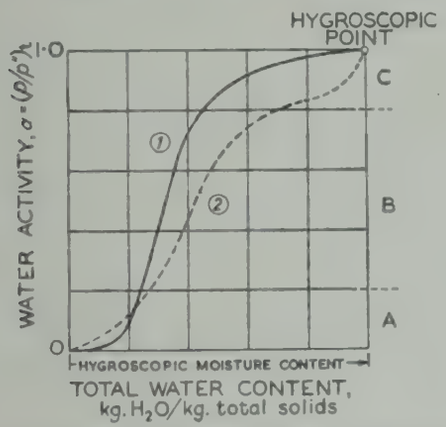

FIG. 2. *Sorption isotherms for colloidal* (1) *and capillary porous colloidal material* (2)
Temp. = constant

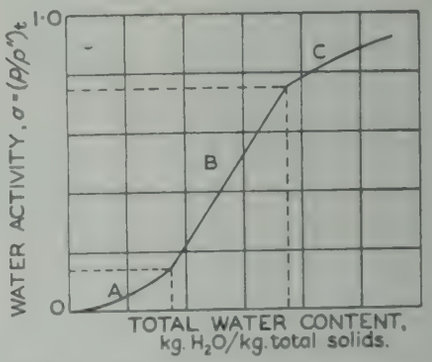

FIG. 3. *Possible course of sorption isotherm for material having ' bound water ' (section A)*

Methods for estimation of ' free water '

For the estimation of ' free water ' in a product the following methods are available:
(*a*) Freezing method (calorimetric or dilatometric).
(*b*) Solvents method for liquids by depression of freezing points or of vapour pressure.
(*c*) Chemical dehydration method (using cobalt chloride, copper sulphate, alcohol).
(*d*) Other methods (vapour pressure method, swelling pressure method, electric method of Higashi).

(*a*) *Freezing methods*

The ' bound water ' is usually defined as that which remains unfrozen even if the sample is submitted to very low temperatures down to -50 or -70°C and which could only be expelled (and determined by weighing) by heating normally to about 105°C. The amount of bound water is considered to be equal to the unfrozen water; the free or frozen-out water is determined *calorimetrically* from the difference of enthalpy (measuring the latent heat of ice melting) or *dilatometrically* from the change in volume of sample taking place due to freezing out water. The freezing method has been used frequently for many different products.

(*b*) *Solvent methods*

For estimating the ' bound water ' in liquids the *depression of its freezing point* after adding a known solution or the *depression of its vapour pressure* can be used. The depression of the freezing point is greater the more bound water there is present in the tested liquid. ' Free water ' in a food will be determined as such, which gives normal vapour pressure depression when a known substance is added to this food.

(*c*) *Chemical methods*

Cobalt chloride hexahydrate ($CoCl_2.6H_2O$) has a pink colour which turns blue when it loses water and becomes pure $CoCl_2$. By adding the hexahydrate to a sample of food and drying it at 25–30°C it is possible to check when the colour turns blue showing that free water is no longer present. The amount of bound water could then be determined by weighing.

Copper sulphate and other substances could be used in a similar way.

(*d*) Many other different methods have been proposed for measurement of the amount of ' bound water,' such as vapour pressure, swelling pressure, electric resistance,* etc., but they have not often been applied. The change in concentration of a good solvent (like sugar) in a solution when it is added to a sample to be tested could be used for estimation of bound water which does not dilute any solvent (method of Dumanski).

In trying to compare the different methods and results obtained by them, it is found that few investigators have given figures suitable for such comparison, but where comparative studies were made[8] it was shown that a remarkable deviation existed not only in results on the same kind of material using different methods of determination of free water, but also when the same method was used. Table III shows some figures emphasizing this point. From the literature results and from the author's investigations the freezing method appears the most reliable and gives quite good reproducible results. By this method the amount of *non-frozen* or *non-freezable water* can be determined with reasonable accuracy.

The recently published results of careful work by Riedel[10–12] are worthy of note.

Fig. 4 shows that, if the results for protein materials are studied, quite good agreement is obtained for the value of non-frozen water content for fish, meat and eggs, and it remains constant when plotted against the total water content. The experiments of Riedel were performed with a very precise calorimeter. They give the same value, 0·4 kg. H_2O kg. protein for non-frozen water, which is changed only when the total water content is decreased below this figure by careful dehydration. Even when much fat is present (as in yolk) the relative amount of non-frozen water remains constant when related to protein. Riedel calculated that one atom in muscle protein binds 2·0 molecules of unfreezable water.[12] This may be different when carbohydrates are present; appropriate experiments are now in progress to elucidate this point.

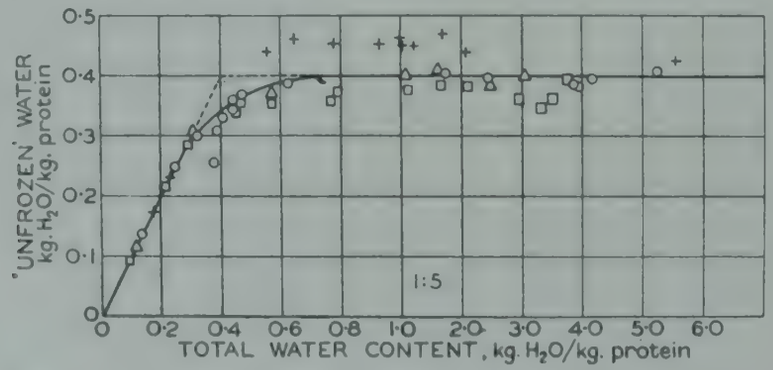

FIG. 4. *' Non-frozen ' water in relation to the ' total water ' content*
O fish Δ egg yolk
□ meat + egg white

Considering the application of the freezing method to protein foods it may be stated that the following processes occur: after sufficient lowering of the temperature the ice starts to crystallize, which leads to concentration of the remaining solution. It is assumed that the ice is formed not only from intercellular liquid but that the protoplasm is dehydrated to some extent too and a part of it may form a gel with ultramicroscopic capillary cavities. Water and

*Electric resistance at 50 cycles decreases with decreasing water content as long as free water is present and after passing a minimum, increases again when only bound water remains in the cells.

Table III

Estimation of ' bound water ' in different foods (experimental results)

Material	Method	Bound water: g. H_2O/g. total solid	Bound water: % of total water	Reference
Myogen	Freezing (−20°)	0·48		9
Egg albumen	,, (−20°)	0·31–0·38		
Gelatin	,, (−20°)	0·53		
Beef muscle	,, (−40°)	0·43		
Frog meat muscle	,, (−40°)	0·45		
Gelatin	$CoCl_2$	max. 0·325–0·35 min. 0·22 –0·28		8
Beef meat, raw (1·6% fat)	Dumanski (adding sugar)	0·42–0·59		7
Beef meat, cooked	,,	(0·35)		
Beef meat, salted	,,			
Hog meat, raw (4·5% fat)	,,	0·37–0·45		
Hog meat, cooked	,,	(0·25–0·3)		
Beef meat, non-ripened	,,	0·35		
Beef meat, aged	,,	0·38		
Strawberries (18 samples)	Freezing (−20°)	0·35		1
Asparagus, tips	,,	0·35	4·0	
Asparagus, butts	,,	0·33	2·6	
Corn (whole grain)*	,,	2·2	33·8	
Green beans	,,	0·11	1·0	
Green beans (com'l)	,,	0·68	5·3	
Lima beans†	,,	0·05	1·3	
Wax beans (pencil pod)	,,	0·16	1·6	
Wax beans (round podded)	,,	0·3	2·5	
Raspberries	,,	0·32	5·8	
Rhubarb	,,	0·04–0·18	0·3–1·4	
Strawberries	,,	0·43	4·7	
Tall telephone peas	,,	0·2 (0·04–0·32)	0·8–6·8	
Fish	Freezing (−70°)	0·385	8–10	10
Fish	,, (−20°)		10–12	10
Beef meat Calf meat Deer meat Chicken meat	Freezing (−70°)	0·35		11
Egg white	Freezing (−70°)	0·45		13
Egg yolk	,, (−70°)	0·40		13
Fish and all meats	Freezing (−70°)	0·4**	—	11

*15% total solids. †28% total solids. **g. H_2O/g. protein.

aqueous solutions adsorbed on the internal surfaces and enclosed will not freeze because of the depression of the freezing point due to lowering of the vapour pressure and sub-cooling effect in the capillaries,[11] and also because of the concentration of dissolved substances in them. Change in pH value should be avoided, but even if it occurs it should not lead to protein denaturation. A coagulation or even denaturation may occur due to the pressure of ice crystals and the effect of strong solutions of electrolytes. When the temperature is sufficiently low the remaining liquid may freeze at the eutectic point. It seems that the water of hydration within the swelling gels, which perhaps could be considered as really ' bound ' to the proteins, will still remain unfrozen. In this case, the amount of bound water will be equal to, or smaller than, the unfrozen water; and the ' non-frozen ' water will be more nearly equal to the bound water as determined experimentally by freezing, the less the amount of water not bound to proteins (e.g., in microcapillaries) remains unfrozen. From experiments shown in Fig. 5 it seems to be evident that either the amount of unbound water remaining unfrozen is very small or this water remains unfrozen even down to the lowest temperature used. Such water should be considered as bound, when determined by freezing or ' bound against freezing.' It may also be called (Luyet[15]) ' unfreezable water.' Luyet's conception of five forms of water present in living tissue was: ' excess water,' ' metabolic water,' ' vital water ' (removal of which is lethal), ' remnant freezable ' (which freezes after death) and ' unfreezable water.'

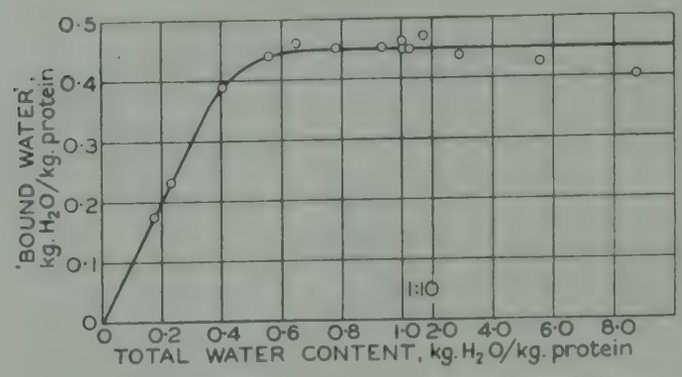

FIG. 5. *' Non-frozen ' water in relation to the ' total water ' content of egg white*

Conclusions

The present knowledge of the possible forms of water binding does not allow any simple explanation of the problem that could be generally accepted as the conception of water in such complex biological materials as foods being in two states, namely as ' free ' and ' bound ' water. There are very strong differentiations to be made as to the strength of these different forms of binding and to their reactions to different means applied to overcome the binding forces, but little is known about the very complex forces which are effective and especially about the influence of different factors on them.

To ensure comparable results it is necessary to use well established and as far as possible the same methods of determination. It seems that even the determination of the value of ' total water content ' as, e.g., measured by dehydration at temperatures over 100°, is not standardized and therefore may lead to non-comparable results. The values are often not consistent because of differences in time–temperature relations and heating rates; this may be caused by coagulation processes or even by an attack on the water forming part of the constitution of the product,[16] e.g., with starch. Here it should be possible to reach international agreement, maybe with some alterations for heat- or acid-sensitive materials.

But even if the ' total water content ' could be measured comparably and reproducibly, then the idea of ' bound water ' may be of use only in connexion with special processes applied to groups of similar foods. In agreement with a similar proposal of Leniger,[17] the term ' free ' water could be applied, not in the sense ' generally free ' independent of the method of its removal, but only as ' restricted free ' and related to some technological or other method of handling of the product under some specified conditions. Having, for instance, the freezing of foods in mind, it may be of considerable interest to establish the limits of ' unfreezable ' water; its determination may give an idea of the changes which may take place during storage of foodstuffs, being an objective indication of irreversible processes leading to loss of quality of frozen products. This means that if during storage there is denaturation of proteins in protein foods, it will probably be possible to estimate the extent of denaturation by measurement of decrease of 'unfreezable water.' But such a method may also be valuable for indication of changes caused by dehydration and during the storage of dehydrated products.

Summarizing the above discussion of the problem on bound water in foods, it may be stated:

(1) It is not possible to give a definition of ' bound water ' in foods which will be generally valid and which can be determined by any known method.

(2) If ' bound water ' is defined as water which is held firmly by the proteins and carbohydrates as hydrophilic colloids for their hydration only, there is no possibility of measuring it separately by any known technique and therefore there is no evidence for its existence.

(3) It seems to be possible to define and use the terms ' free ' and ' bound ' water in connexion with exactly prescribed methods of handling of the food, having in mind, e.g., water free for dehydration, freezing, etc.; but it might be better for precise purposes to call such ' bound water ' as water ' bound against dehydration ' or ' bound against freezing,' etc.

(4) It seems to be sensible to define as ' unfreezable water ' in protein foods the water which remains unfrozen at temperatures below —30°C and to relate it to the protein content of these products only; the term ' free water ' may then be understood as ' water free to be frozen.'

(5) A correlation between the amount of ' unfreezable ' water and of water not absorbed by cobalt chloride or other chemicals has still to be checked; the same is valid for other methods as far as proposed for determination of ' bound water.' There seems to be no evidence that such a correlation does exist and is valid for all foods.

(6) The assumption that an attack on ' unfreezable water ' in the food leads to irreversible changes has still to be proved; if it is true the estimation of the amount of ' unfreezable water ' may give an objective indication of irreversible changes during processing like dehydration, freezing, etc., and storage of foodstuffs.

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THE SORPTION OF WATER BY HAEMOGLOBIN

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The adsorption of water on freeze-dried haemoglobin (ox) and alcohol-denatured haemoglobin (ox) has been followed by the weighing-bottle and salt solution method. Even after seven months, a hysteresis loop was still apparent, and of the two branches, the adsorption branch gave the closest fit to the B.E.T. equation. The monolayer values corresponded to adsorption of water on about 73% of the polar side-chains, probably spread out over the surface of the molecule, regarded as a prolate spheroid 45 Å × 45 Å × 65 Å. Differential and integral heats and entropies have been calculated by an application of the methods of Hill *et al.* to the adsorption branches of the isotherms. These results support the ' freezing ' of water molecules on localized sites fairly well separated on the molecular surfaces, and there is a clear decrease of integral entropy to a minimum over the complete monolayer. The fact that this behaviour is not observed in silk fibroin may be due to entropy contributions from the chain segments.

Introduction

The adsorption of water vapour on crystalline proteins was studied by Bull,[1] Shaw[2] and Pauling,[3] the first author providing B.E.T. isotherms[4] for an extensive series of proteins which gave a great stimulus for later work. Two definite views emerged concerning the number of water molecules in the B.E.T. monolayer: (*a*) Shaw[2] found for egg albumin that the area of the B.E.T. monolayer area was 210–220 m.²/g., close to the area of the intermolecular polar surfaces of 225 m.²/g., suggesting that water molecules penetrated the crystal to be adsorbed on these surfaces. Bull[1] also favoured this idea. (*b*) Pauling[3] found that the adsorbed water molecules corresponded roughly to the number of polar side-chains in the protein, suggesting that water molecules penetrated throughout the molecules to be adsorbed on the side chains. McLaren & Rowen[5] suggested that these two equalities mean that the intermolecular interfaces are made up of polar groups. Sponsler *et al.*[6] considered that water-adsorbing groups of proteins could be classified as polar side chains or as peptide bonds. Pauling's view that adsorption on peptide bonds could generally be ignored was based on the small water adsorption observed for nylon. It was suggested that adsorption was prevented by intermolecular hydrogen bonds. There is, however, evidence for adsorption on the peptide link in diglycylglycine[7] and polyglycines,[8] and the question remains open.

The differential heats and entropies of adsorption of water molecules on proteins were calculated by Bull,[1] Dole & McLaren,[9] and Davis & McLaren.[10] Strongly negative entropies of adsorption observed for silk and wool indicated a localization of water molecules on polar groups in agreement with the Pauling model, while the positive entropy values observed in some cases, such as crystalline egg albumin and lyophilized lactoglobulin, were thought to point to configuration changes induced in the protein.[10]

Further studies on B.E.T. isotherms have been made by Benson and co-workers, using non-polar[11, 12] and polar[13, 14] gases. While the former gases measured the external areas of the crystalline particles, the polar gases penetrated the crystals in the same way as water. Benson *et al.* discussed the hysteresis found for water[15] and other polar gases,[16] correlating it with the number of basic side chains in the proteins.

No studies have so far been reported on proteins containing prosthetic groups. Haemoglobin, which falls into this class, is the subject on an intensive *X*-ray crystallographic investigation by Bragg *et al.*[17, 18] Thus, the haemoglobin molecule is known to be a tilted prolate spheroid, and when the crystals adsorb water only the intermolecular spacings change and there is no effect on the internal distances within the haemoglobin molecule. The dimensions of the molecule in the fully hydrated state is 53 × 53 × 71 Å and in the dry state, 45 × 45 × 65 Å. Since the diameter of a water molecule is 2·8 Å the difference must correspond to at least a double layer of water molecules around each haemoglobin molecule at saturation, which is reasonable. The present work establishes a fairly accurate value for the *monolayer* coverage, allowing deductions about the distribution of polar groups in the molecular surface. In addition, molar differential and integral entropies and heats of adsorption of water molecules have been calculated according to equations given by Hill[19, 20] and applied in a practical case by Hill *et al.*[21] In the case where molecules are strongly bound to the surface, a minimum in the molar integral entropy of adsorption is to be expected on completion of the B.E.T.

monolayer, owing to loss in the number of configurations.[22] This forms a diagnostic test for localized adsorption. The equations for the heat content and entropy are:

Differential values, H_s, S_s,

$$\left(\frac{\partial \ln x}{\partial T}\right)_\Gamma = \frac{H_{L'} - \bar{H}_s}{RT^2} = \frac{S_{L'} - \bar{S}_s}{RT} - \frac{\ln x}{T} \quad \ldots\ldots(1)$$

Integral values, H_s, S_s

$$\left(\frac{\partial \ln x}{\partial T}\right)_\varphi = \frac{H_{L'} - H_s}{RT^2} = \frac{S_{L'} - S_s}{RT} - \frac{\ln x}{T} \quad \ldots\ldots(2)$$

Here $x = p/p^0$ is the ratio of pressure to saturation pressure of the water, Γ is the ratio of moles of water adsorbed, N_s, to the number of moles of adsorbent, N_a, i.e. $\Gamma = N_s/N_a$. S denotes entropy, H heat content and the subscripts L′ liquid water and $_s$ adsorbed water. The spreading pressure φ of the adsorbed water is given by Bangham's equation (derived from Gibbs' adsorption equation),

$$\varphi = \frac{RT}{N_a}\int_0^x \frac{N_s}{x}\,dx \quad \ldots\ldots(3)$$

These quantities are therefore net entropies and heat content changes for the process of transferring a g.-mole of water molecules from the pure liquid to the adsorbed state.

Experimental

The determination of surface pressure, φ, by equation (3) requires a summation of the area under the curve of $N_s/N_a x$ plotted against x, and this in turn requires accurate values of the amount of adsorption N_s/N_a down to low values of the relative pressure x, to ensure an accurate extrapolation to $x \to 0$.

In the first place, a succession of measurements of Γ were carried out at increasing x values over the range $x = 0{\cdot}001$ to $0{\cdot}09$, using one sample of haemoglobin in a silica-spring adsorption balance of the well-known McBain–Bakr type. Even using finely powdered haemoglobin or a porous alcohol-denatured haemoglobin, it was found impossible to reach equilibrium for a single point on the isotherm within one week. Since it was hoped to determine twenty or more points it was decided to abandon the method. Clearly, the rate of diffusion of water vapour within the haemoglobin crystal is too slow at these very low pressures, and in the subsequent application of the 'weighing-bottle and salt solution method'[5] a series of tests confirmed this conclusion. A total of 160 tubes was made up, each containing a separate weighed sample of haemoglobin sealed over a solution of sulphuric acid chosen to give a predetermined relative vapour pressure x. The tubes were held for 7 months in a thermostat controlled to $\pm 0{\cdot}1°$, after which the tubes were opened and the haemoglobin sample weighed, dried in air for 3 days at 110°, and weighed again, thus obtaining Γ. Comparative tests showed this method gave a dry weight about 0·2% less than that obtained by drying over P_2O_5 *in vacuo*. A third weighing of the solution gave water loss, leading to the true concentration of sulphuric acid from which was calculated the x value at equilibrium in the tube. Eight separate series of 20 tubes were equilibrated, as below, and the 20 x values lay in the range of 0·0004–0·80.

Freeze-dried haemoglobin (Hb) (1) adsorption, at 30°.
(2) desorption, at 30°.
(3) adsorption, at 40°.
(4) desorption, at 40°.

Series (5), (6), (7) and (8) were a repetition of the above using alcohol-denatured haemoglobin.

The adsorption runs started with haemoglobin that had been dried at room temperature over P_2O_5 *in vacuo*. The desorption runs started with haemoglobin in the 'wet state' obtained by keeping a sample in a closed vessel over water.

The haemoglobin used in this work was prepared from fresh ox blood. The red cells were separated, washed four times with 0·9% NaCl solution, followed by dialysis against tap water for 12 hours during which process haemolysis occurred. The dialysis was continued for at

least 48 hours against distilled water until chloride ion was undetectable by silver nitrate. The stroma were removed by shaking with 30% (v/v) ether followed by centrifugation, the lower layer containing the haemoglobin being sucked off into a suitable vessel. A trace of silicone was added to this solution to prevent frothing, and it was then evacuated in a desiccator to remove ether and oxygen. To prepare freeze-dried material the solution was frozen at −80° in a 250-ml. spherical flask and pumped via a cold trap by a two-stage Speedivac pump. A single large preparation was divided into eighty specimens for the above experiments. The alcohol-denatured preparation was made by precipitation of a solution of haemoglobin with methyl alcohol.

Results

The adsorption isotherms are given in Figs. 1 and 2. True water adsorption is expressed as % regain, calculated on the dry weight as defined earlier. It is possible that Bull's method of drying, for 24 hours in a vacuum oven at 105°, would give a slightly different result from that obtained here, but it is not possible to define precisely the dry state of a protein, as was pointed out by Bull.

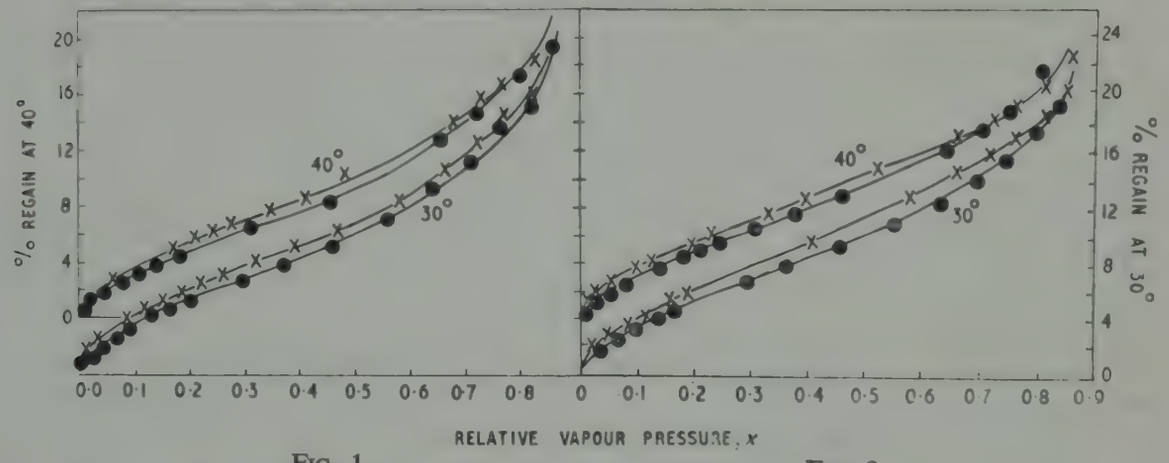

FIG. 1. FIG. 2.

FIG. 1. *Adsorption (●) and desorption (×) isotherms of water on freeze-dried haemoglobin*

FIG. 2. *Adsorption (●) and desorption (×) isotherms for denatured haemoglobin*

In Figs. 3 and 4 the data have been replotted in terms of the B.E.T. equation[4]

$$\frac{x}{V(1-x)} = \frac{1}{V_m C} + \frac{(C-1)}{V_m C}\, x$$

where $x = p/p_0$ and V is the amount of adsorbed water expressed as g. per 100 g. of dry protein. The points in Figs. 3 and 4 are not experimental points, but have been taken from the smoothed curves drawn through the original points of Figs. 1 and 2. Careful scrutiny shows that the desorption points show a definite deviation from linearity, but the adsorption points fit a line over the range 0·05 or 0·10 to 0·30. The C values fall in the range $8{\cdot}7 \pm 1{\cdot}4$ and the monolayer coverages, V_m, based on the two straight lines through the adsorption data, are:

	V_m, g./100 g. protein		Mean V_m, mole/g.
	30°	40°	
Freeze-dried Hb	5·76	5·72	0·00319
Denatured Hb	5·52	5·48	0·00306

In Figs. 5 and 6 are plotted the integral and differential heat content changes, and the integral and differential entropy changes, for the adsorption from liquid water of one mole of water molecules, on the protein. The methods of Hill *et al.*[21] were applied to the adsorption branches of the isotherms to calculate these data.

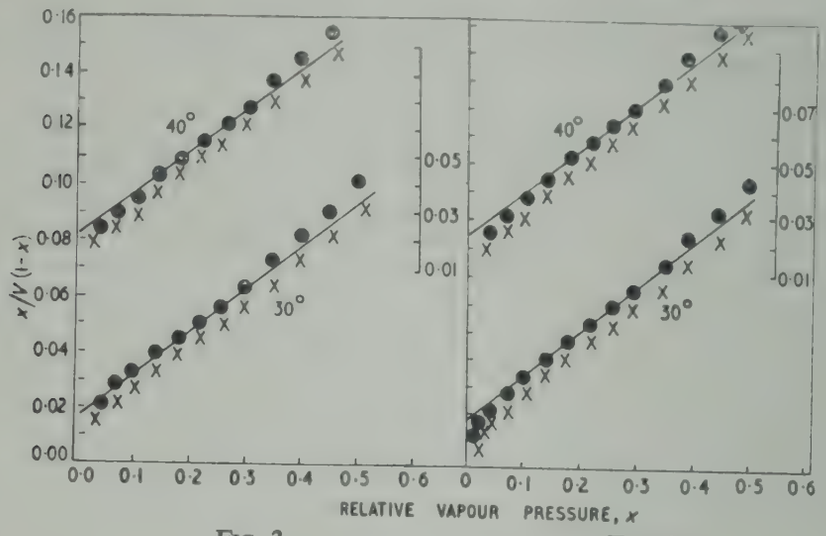

FIG. 3. FIG. 4.

FIG. 3. *B.E.T. plots for the isotherms of Fig. 1 for freeze-dried haemoglobin*

FIG. 4. *B.E.T. plots for the isotherms of Fig. 2 for denatured haemoglobin*

(The lines in each case are drawn through the adsorption points)

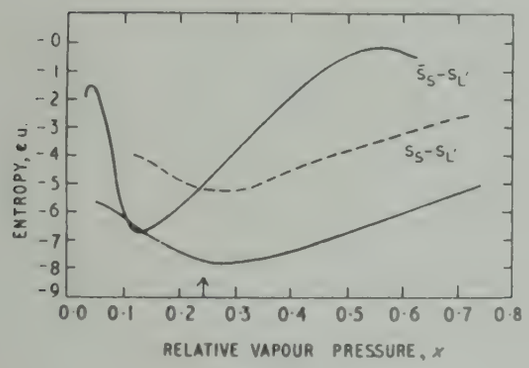

FIG. 5.

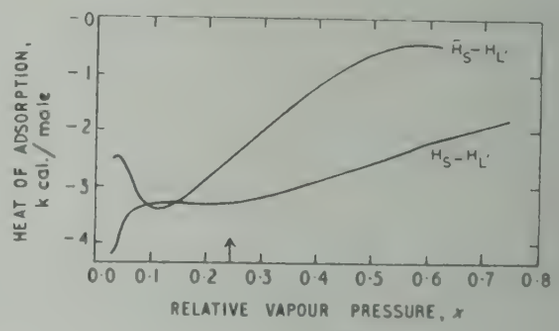

FIG. 6.

FIG. 5. *Integral and differential entropies of adsorption of liquid water on freeze-dried haemoglobin, calculated from the adsorption isotherms of Fig. 1*

FIG. 6. *Integral and differential heats of adsorption of liquid water on freeze-dried haemoglobin, calculated from the adsorption isotherms of Fig. 1*

(Arrow indicates B.E.T. monolayer)

Discussion

It is of interest in the first place to consider the V_m value of 319 moles of water per 10^5 g. of protein in terms of the surface area and polar side-chain content of the haemoglobin molecule. First is calculated the number of water molecules which would occupy a saturated monolayer over the whole haemoglobin molecule. The area of this molecule will be that of the ' dry spheroid ',[17] namely 8349 Å^2, and taking the cross-section of the water molecule[23] as 10·6 Å^2, this gives 788 water molecules in the close-packed layer. Since the molecular weight of haemoglobin is 68,000,[24] there are $8{\cdot}86 \times 10^{18}$ haemoglobin molecules per g. and so the calculated amount of adsorbed water, for a monolayer covering all the intermolecular surfaces, will be 1160 moles per 10^5 g. of protein, which is nearly four times greater than the observed amount.

The total number of polar side chains, including proline, for horse haemoglobin is 435·1 moles per 10^5 g. of protein.[25] This number is still larger than the observed water adsorption, and the difference may be compared with the very close correspondence found by Pauling[3] for silk, namely, 226 adsorbed moles and 228 polar side-chains. The haemoglobin figures therefore suggest that water adsorption occurs only on polar side-chains actually in the molecular surfaces, and that these form a fraction of about 73% of the total polar side-chains in

the molecule. The presence of most of the polar side-chains in the molecular surface, in this way, is in accord with the crystallographic evidence that liquid water fails to penetrate within the haemoglobin molecule itself.

The entropy curves in Fig. 5 are consistent with the relatively successful fit of the B.E.T. equation to the adsorption branch of the curves. Thus, where the gas molecules are held by sufficiently strong forces to give localized adsorption on the surface, a minimum in the integral entropy curve and a point of inflexion on the differential entropy curve are expected at the completion of the monolayer, due to loss in the number of configurations of the adsorbed molecules as the monolayer tends to completion,[21, 22] The entropy data agree with this prediction, within the accuracy of experiment, and therefore give definite support to a model involving localized adsorption on polar side-chains distributed over a surface. Furthermore, since the entropy of fusion of ice is only 5·26 cal./deg. mole the actual value of the observed entropy supports the idea of localized adsorption of water molecules. The only discrepancy in the thermodynamic arguments arises in comparing the differential and integral quantities, in particular, the entropies. These must be *equal* whenever the integral entropy passes through a maximum or minimum; since if S_s be the entropy of the system of N_s moles of adsorbed water

$$S_s = N_s S_s,$$

$$\text{and } \bar{S}_s = \left(\frac{\partial S_s}{\partial N_s}\right)_{A,T} = S_s + N_s \left(\frac{\partial S_s}{\partial N_s}\right)_{A,T}$$

$$\text{so when } \left(\frac{\partial S_s}{\partial N_s}\right)_{A,T} = 0, \quad \bar{S}_s = S_s.$$

A part of this discrepancy may reside in the failure to achieve complete equilibrium, the full significance of the hysteresis loop being uncertain. A definite error also attaches to the integral entropies, since the failure to obtain accurate adsorbed quantities at low pressures affects the accuracy of the integrations used to obtain surface pressures. To satisfy the above thermodynamic criterion, by moving the integral entropy curve, it would be necessary to raise it by 2·5 cal. deg.$^{-1}$ mole^{-1} to the position shown by the dotted line in Fig. 5.

Summarizing, the above considerations suggest that V_m corresponds to 217 molecules of water adsorbed on polar side-chains spread over the surface of the haemoglobin molecule of 8349 Å^2. If the adsorbed molecules are spread out uniformly on a square lattice this corresponds to spacing between the water dipoles of $a = 6{\cdot}2$ Å. Topping[26] gives for the mutual electrostatic potential energy per dipole, of parallel oriented dipoles

$$W = \tfrac{1}{2}\frac{\mu^2}{a^3} \cdot \frac{9{\cdot}0336\, N^0}{4{\cdot}18 \times 10^7} = 0{\cdot}93 \text{ kcal./mole.}$$

Substituting a value of 1·85 D for the dipole moment μ gives the value above, per mole of dipoles. The result for a triangular lattice is only 20% larger, so we may assume that a total drop in integral exothermic heat of adsorption $-(H_s - H_L')$ of about 1 kcal./mole occurs from dipolar repulsion on forming the monolayer. Reference to Fig. 6 shows that values for $H_s - H_L'$ are not available at the lowest coverages, and it is not clear how far the first few adsorbed water molecules are held on specially 'strong' sites. There is, however, an observed decrease of perhaps 0·8 kcal./mole in heat between $x = 0{\cdot}03$ and 0·10, i.e. very roughly between 10% and 40% of the monolayer coverage. From 40% to 100% of the monolayer the integral heat remains constant at about −3·4 kcal./mole. The observed decrease in heat of adsorption is thus of the right amount to be explained by dipolar interaction, but it is perhaps surprising that it does not occur more uniformly as the coverage increases.

It is generally more accurate to derive heats from calorimetric data than from the Clapeyron–Clausius equation, and Dunsford & Morrison[27] have combined their measured heats of wetting of silk fibroin with the isotherm of Hutton & Gartside[28] to derive differential and integral entropies of adsorption of water on to this protein. Their calculation has now been repeated, but using the equation of Jura & Hill[22] for the integral molar entropy change on adsorption

$$S_S - S_L' = \frac{(E_S - E_L')}{T} + \frac{\varphi}{\Gamma T} - R \ln x.$$

The term in brackets is the measured heat of wetting, while φ/Γ was estimated from the data of Hutton & Gartside. The result was a curve with a broad minimum, with $S_S - S_{L'} = -3$ cal./deg. mole for $0{\cdot}2 < x < 0{\cdot}7$. There was no sign of a minimum in entropy at the B.E.T. monolayer such as has been found for haemoglobin. It seems possible that since water molecules must penetrate between individual polypeptide chains to reach *all* the polar groups of the silk fibroin (as demonstrated by Pauling) the simple decrease in entropy following loss in the number of configurations of water molecules will be obscured by positive entropy contributions from increasing segmental chain movements. In this connexion it may be significant that the value of -3 cal. deg.$^{-1}$ mole^{-1} for the broad minimum in silk fibroin is appreciably more positive than the 'corrected' value of -5 cal. deg.$^{-1}$ mole^{-1} for haemoglobin from the dotted curve in Fig. 5.

In considering the causes of hysteresis in the haemoglobin isotherms, it is known[13] that the presence of air slows down the rate of uptake of water by proteins by several orders of magnitude, but there is also a true hysteresis which is found to be virtually independent of temperature for bovine serum albumin. Seehof *et al.*[16] have attributed this hysteresis to binding of water molecules on the free basic groups of the protein causing a non-reversible swelling. The results of the present experiments show that the hysteresis for haemoglobin is, in fact, slightly larger at the lower temperature, and also that the hysteresis is rather more marked in denatured than in freeze-dried haemoglobin.

To conclude, the experimental results support the view that the water molecules are localized on polar groups spread over the surface of the haemoglobin molecule. About 73% of the total polar side-chains are involved and these are probably spaced out fairly evenly. Differential and integral entropy and heat calculations support this picture, but there is some hysteresis so that thermodynamic data must be received with some caution. The silk fibroin system presents a different picture, in accordance with other evidence that water molecules penetrate between the polypeptide chains.

Acknowledgment

The authors gratefully acknowledge a grant from the Department of Scientific and Industrial Research (Food Investigation) to M. H. C., which made this work possible.

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Discussion on preceding two papers

Dr. N. Uri: In general I am in agreement with those speakers who pointed out that there is continuity in the strength of water binding; yet from a practical point of view it is advantageous to draw a line in the course of dehydration. This line is best placed where dehydration affects polar groups, molecules, and ions, particularly trace metals. Denuding trace metals of their hydration shells is bound to affect their oxidation–reduction potentials, their reactivity in electron-transfer reactions and hence their catalytic activity in inducing the aerobic oxidation of unsaturated fatty acids, which in my view is always in its very early stage initiated by free radicals produced in electron-transfer reactions (or conceivably hydrogen transfer reactions) involving trace metals. Experiments which were carried out in our laboratory suggest an intimate connexion between the activity of trace metals as oxidation catalysts and the polarity of environment. Oxidative rancidity (during subsequent storage) sets in abruptly at a certain stage of dehydration; this is in agreement with the above hypothesis.

Prof. D. D. Eley: On the face of it, Dr. Uri's suggestion that the first adsorbed monolayer of water will have the largest effect on the reaction velocity of a substrate seems very reasonable; but the hydrogenase activity of *Esch. Coli*, as measured by the pH_2 change, which is lost on dehydration of the bacteria, is in fact only restored completely by addition of 3 mg. of water/mg. of dry weight of bacteria, which is greatly in excess of the monolayer value.[1] The problem here may be structural, i.e., only when the cell is completely filled with water is the system exposed with its right spatial relation.

I suggest that the B.E.T. monolayer value might be taken as a rule-of-thumb measure of bound water, although I agree the measurements require time and their interpretation will be obscure for heterogeneous surfaces.

Dr. B. P. Fish: There is a thermodynamic relationship between the lowering of the vapour pressure (p_1/p_0) and the freezing point depression (ΔT) and, to a first approximation, $\log_{10}\frac{p_1}{p_0} = -\frac{1{\cdot}15\Delta T}{273-\Delta T}$. 'Bound' water which will not freeze at $-30°$ is in equilibrium with an atmosphere of activity less than 0·70. (This explains why all the water cannot be frozen in a foodstuff even at very low temperatures.) The observations of P. Girard and P. Abadie (*Disc. Faraday Soc.*, 'Dielectrics,' 1946, p. 46), may be relevant. They examined the absorption spectrum of maize starch and gluten in the microwave region, and their concept of 'free' water had an absorption band at 1 kcs while 'bound' water absorbed at 3 Mc s frequency. One may generally say that 'free' water in any material is thermodynamically similar to ordinary water at a similar temperature and pressure; and 'bound' water has different thermodynamic properties.

Prof. Kuprianoff: I agree with Dr. Uri that it would be advantageous to have a 'line' in the course of dehydration; but I would like to remind you that all proposals given today for such a limit as a possible measure of bound water are specifically defined by the method of measurement and do not give the real value of what could be accepted as a general valid term for bound water. Therefore, each suggestion for definition of 'bound water'—and even the best one—needs for its general acceptance some kind of international agreement, but we have not succeeded in getting even a generally accepted definition and method for determination of the water content of foodstuffs.

I would like to thank Dr. Fish for his remark, concerning the publication of P. Girard and P. Abadie; I did not include their proposal for the definition of bound water as I had no knowledge of this paper.

Dr. Eley: I should like to add that if the entropy of the adsorbed water molecules is simply determined by the number of configurations on a set of fixed sites of equal energy, then as $x \to 0$ (and the coverage therefore tends to zero also) both differential and molar integral entropies of adsorption will tend to $+\infty$.[1] If we accept the indications of Fig. 5 this is not so, the results suggesting that the first water molecules are bound very tightly on a few sites of high energy. This would parallel our comments in the paper concerning the observed heat content changes. Our results are not accurate enough, however, properly to establish the point, which could be important in practice, and I raise the matter to show the need for obtaining greater accuracy in the adsorption isotherms at very low relative vapour pressures.

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SESSION II

Chairman : Prof. J. Kuprianoff

SOME PROPERTIES OF AIR IN RELATION TO DEHYDRATION

By PROF. A. W. SCOTT
(*Royal College of Science and Technology, Glasgow*)

Introduction

The aim of this paper is to review available data on the properties of dry and humid air. Reliable data are not lacking for the properties of dry air and of steam. In the case of air, the molecular theory of gases—which relates the transport properties and equation of state to intermolecular forces—has been applied to the correlation of existing experimental data. The properties of steam, certainly over the range of interest in dehydration, are also well established. Unfortunately, however, the properties of humid air have not been studied in the same exhaustive manner and since neither air nor water vapour behave as ideal gases, a certain amount of conjecture has still to be used in humid air calculations.

The properties normally required in industrial calculations are specific heat and enthalpy and also specific volume, all commonly expressed per lb. of dry air. In addition, the more detailed scientific aspects of dehydration involving the study and correlation of mass- and heat-transfer aspects require a knowledge of such properties as viscosity and thermal conductivity.

Properties of air and water vapour

Comprehensive tables of properties of air and water vapour, among other gases are given in Circular 564 (1955) of the National Bureau of Standards,[1] and most of the data given in Figs. 1 and 2 of the present paper have been obtained from this publication. The properties of air were correlated by the virial equation of state

$$Z = PV/RT = 1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} \qquad \text{(1)}$$

where the virial coefficients, B, C and D, are temperature-dependent functions. Data for steam were based on the equations of Keyes.

For ideal gases the compressibility Z is unity. Actual values of Z for air and water vapour are given in Circular 564 and the following are typical values in the temperature rage of interest in drying.

	Air		Steam
Pressure, atm.	0·4	1·0	1·0
Temp., °F			
100	0·99991	0·99978	
224			0·98591
500	1·00014	1·00036	0·99674

For this temperature range it will be seen that the error involved in treating air as a perfect gas is less than 0·5%. Zimmerman & Lavine,[2] however, apply with commendable thoroughness the Beattie–Bridgman equation of state for the calculation of specific volume of dry air in their psychrometric tables. Quite large errors are involved if water vapour is treated as an ideal gas but, fortunately, the exact value of specific volume can be readily obtained from steam tables for saturated and superheated steam.

It has been common practice in drying calculations to assume a constant specific heat, usually 0·24, in obtaining the enthalpy of air, but reference to Fig. 1 will show that this may give quite large errors, particularly at higher temperatures. The specific heat at constant pressure varies from 0·24 at 40°F to 0·25 at 580°F. For a given temperature there is little change in specific heat at pressures below one atmosphere. Din[3] uses rather lower specific heat values, but it is suggested that the enthalpy of dry air should be calculated on a mean specific heat for the temperature range concerned, using the c_p curve of Fig. 1.

The enthalpy of water vapour should be taken from steam tables. Frequently, in psychrometric tables, the enthalpy, in B.Th.U./lb. at t°F is taken as $1061 + c_p(t - 32)$, which is reasonable provided that (*a*) the correct mean value of c_p is used and (*b*) the vapour is superheated. Two curves of c_p for water vapour are given in Fig. 2. The upper curve is derived from the data in Circular 564[1] for steam at 1 atm. and shows a minimum value at about 380°F

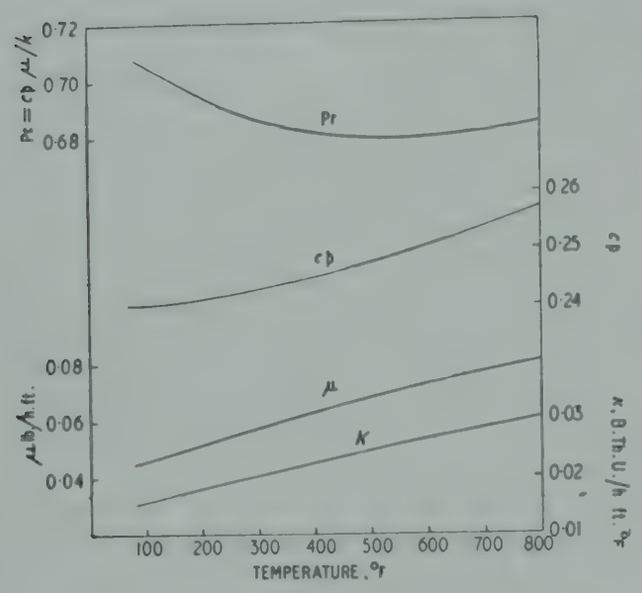

FIG. 1

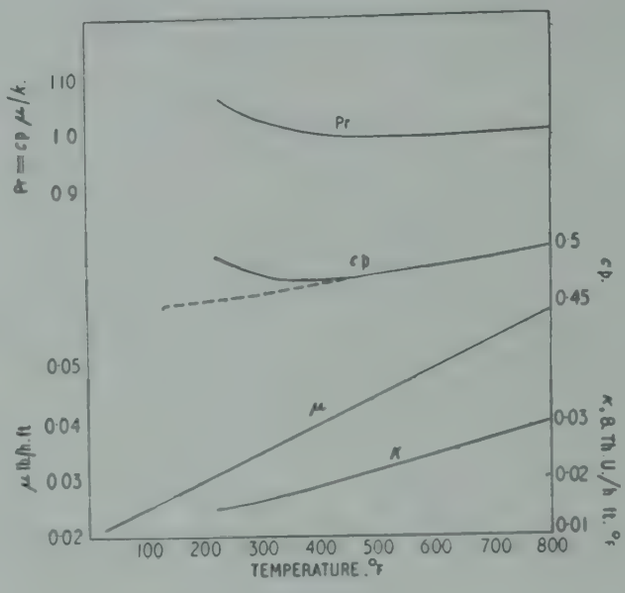

FIG. 2

FIG. 1. *Values of specific heat* c_p; *viscosity* μ; *thermal conductivity* k *and Prandtl No. for dry air at* 1 *atm. pressure*

FIG. 2. *Value of specific heat* c_p; *viscosity* μ; *thermal conductivity* k *and Prandtl No. for water vapour at* 1 *atm. pressure*

The lower dotted curve is for steam at 1 lb. per sq. in. abs., obtained from Keenan & Keyes' Steam Tables. The two curves merge above 500°F. The lower curve has been included as it represents conditions more likely to be encountered in dehydration cal ulations where the partial vapour pressure is small relative to the partial air pressure. The increase at the lower temperature in the specific heat of water vapour, at 1 atm. pressure, may be taken as an indication of the increasing departure from ideality in the gas behaviour as saturation is approached. This effect will be less marked at lower pressures.

Discussion of the laws of heat- and mass-transfer applicable to dehydration is outside the scope of this paper but reference may be made to some of the properties involved. Viscosity enters into the Reynolds, Prandtl and Schmidt numbers, and Circular 564 values[1] for the viscosity of air and water vapour are given in Figs. 1 and 2. Curves of conductivity and Prandtl No. have also been added. Until recently it was commonly assumed in heat-transfer calculations that Prandtl No. for gases are approximately constant, e.g., for water vapour and air the respective values used were 0·78 and 0·74. More exact determinations of conductivity and viscosity are now available and it will be seen from Figs. 1 and 2 that Prandtl No. for steam or water vapour at 1 atm. is substantially unity, and for air is just under 0·7.

Properties of mixtures of air and water vapour

The total pressure of a mixture of gases or vapours must be the sum of the partial pressures exerted by the components, i.e., $P = p_a + p_s$, where P is total pressure and p_a and p_s are respectively the partial pressures exerted by the air and water vapour present. For air saturated with water vapour, p_s is the saturation steam pressure at the mixture temperature, but for partially saturated air this does not hold as the vapour is then superheated.

By Dalton's law, the specific volume V of the mixture per unit mass of dry air is given by

$$V = \frac{RT}{M_A p_a} = W.\frac{RT}{M_s p_s}$$

If the molecular weights of air and water vapour are taken as 28·97 and 18·02 respectively, the mass of vapour per unit mass of dry air is then, $W = 0{\cdot}622\ p_s/p_a$.

Alternatively, if W is known, the specific volume of the mixture is calculable from Amagat's law of additive volumes, i.e., $V = V_a + WV_s$ where V_a and V_s are the specific volumes of dry air and vapour respectively at the total pressure and temperature of the mixture.

Neither of these laws is strictly applicable to air–water vapour mixtures since both are non-ideal gases. In our present state of knowledge, however, Amagat's rule with V_s taken from

steam tables is the more accurate. Various other rules for the specific volume of mixtures have been advanced, but the greatest need is for accurate experimental data relating to air–water vapour mixtures, a field of research which has been neglected hitherto.

A similar degree of uncertainty exists in the calculation of enthalpy for the mixture. Commonly it is assumed that the separate enthalpies of the components, calculated as above, are additive, and this is probably sufficiently accurate for most practical purposes. A possible alternative method is to apply the virial coefficients of the components to derive the specific heat of the mixture. The sensible heat of the mixture could then be calculated and the enthalpy obtained by adding the appropriate latent heat. The derivation of mean specific heats using virial coefficients is a lengthy process but is worthy of further examination. Similar methods can be applied to the estimation of the viscosity of a two-component gaseous mixture. There is no corresponding rigorous theory for the thermal conductivity of a mixture but an empirical method is suggested by Hirschfelder, Curtiss & Bird.[4]

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CALCULATION OF COMPRESSIBIILTY FACTOR AND SPECIFIC HEAT OF AIR—WATER VAPOUR MIXTURES

Note by R. W. BAIN and J. S. BATEMAN (D.S.I.R., East Kilbride)

Experimental data for air–water vapour mixtures are scarce and these notes indicate one method by which they can be obtained. For any fluid the compressibility factor can be written in the form of an expression:

$$PV/RT = 1 + \mathrm{B}(T)/V + \mathrm{C}(T)/V^2 + \ldots\ldots$$

where P, V, T are pressure, volume, temperature and R is the gas constant. For low pressures, all but the first two terms on the right-hand side may be neglected, so that:

$$PV/RT = 1 + \mathrm{B}(T)/V$$

In this, $\mathrm{B}(T)$ is called the second virial coefficient. This may be converted to a series in P and then

$$PV/RT = 1 + \mathrm{B}(T).\mathrm{P}/RT$$

For a mixture $\mathrm{B}(T)$ can be shown by statistical mechanics to be expressible in the form:

$$\mathrm{B}(T) = \sum_{\alpha=1}^{\nu} \sum_{\beta=1}^{\nu} \mathrm{B}_{\alpha\beta}(T)\, x_\alpha x_\beta$$

where

ν = number of components in the mixture

x_α = mole fraction of component α, etc.

$\mathrm{B}_{\alpha\alpha}(T)$ = second virial coefficient for the pure substance, α, etc.

$\mathrm{B}_{\alpha\beta}(T)$ = second virial coefficient corresponding to interactions between molecules of components α and β, etc.

The virial coefficients can be calculated from expressions representing the intermolecular forces. These expressions involve a number of parameters which can be fixed to agree with existing experimental data in the case of pure substances, and simple relations exist for deriving equivalent parameters for dissimilar molecules. A number of these are tabulated in 'Molecular theory of gases and liquids' by Hirschfelder, Curtiss and Bird (reference [4] above).

Using these relations, the virial coefficients and hence compressibility factors for a number of air–water vapour mixtures have been calculated for 1 atm. The results are shown on the attached graphs (Figs. 1 and 2).

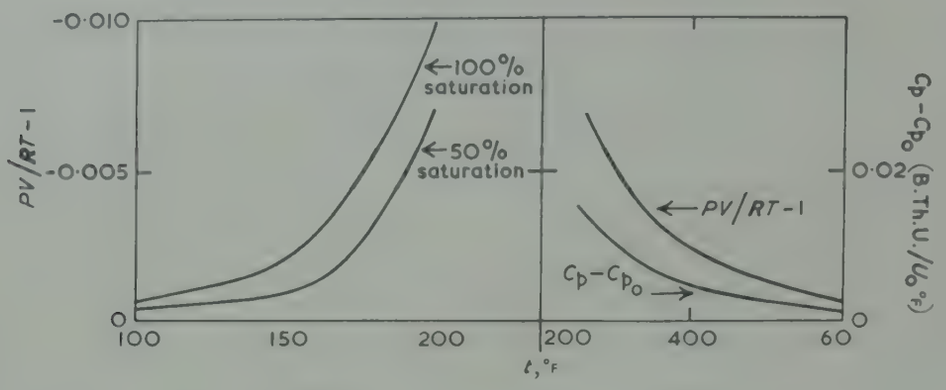

FIG. 1. FIG. 2.

FIG. 1. *Air–water vapour mixtures variation of compressibility factor with temperature for constant percentage saturation*

FIG. 2. *Variation with temperature of compressibility factor and excess of specific heat at constant pressure over low pressure value*
constant mixture
3 g. water, 1 g. air
(saturated at 202·5°F)

It may also be shown that:

$$C_p - C_{p_o} = -PT.\frac{d^2B}{dT^2}$$

where C_p is the specific heat at constant pressure and C_{po} is the corresponding value at 'zero' pressure. This has been calculated for one mixture and is also shown in Fig. 2.

SOME MATHEMATICAL DIFFUSION STUDIES RELEVANT TO DEHYDRATION

By J. CRANK
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Introduction

From the present point of view it is convenient to divide foodstuffs into two main classes: those which can be considered as homogeneous swollen gels in which moisture moves to the surface during drying by a single diffusion process, and those which are permeated by a system of permanent, interconnecting pores or capillaries. Foodstuffs of the second kind are essentially two-phase systems in which transfer of moisture may occur in a number of ways. In this paper, some of the mathematical work on diffusion in both classes of substance which seems to have some relevance to dehydration is reviewed.

Diffusion in homogeneous gels

In the laboratory it is usual to express rates of uptake or loss of moisture in terms of a diffusion coefficient, which for most foodstuffs is likely to be dependent on moisture content. Much mathematical work in recent years has been devoted to the solving of the diffusion equation for such variable diffusion coefficients, and also to the reverse problem of extracting the diffusion coefficient and its moisture-dependence from over-all rates of uptake of moisture or of dehydration. The experimental values required for the latter problem are the amount of moisture entering or leaving a plane sheet of material suspended for various times in an atmosphere of constant humidity. If the experiment is repeated for different humidities, the resulting family of curves relating uptake or loss with time can be analysed to yield the relationship between the diffusion coefficient and moisture content. If both uptake and loss curves can be observed, it is a very simple matter to calculate this relationship from the means of the half-times of the two curves for different humidities (or from the means of their initial gradients if they are plotted against the square root of time). Theoretical calibration curves are also available which allow the diffusion coefficient dependence to be easily extracted from either moisture sorption or dehydration measurements alone if the dependence is of an exponential or a linear kind. A mathematical technique has also been developed for the general case but involves a somewhat laborious trial and error procedure.[1, 2]

From the commercial point of view it is probably more useful to predict the time required to dehydrate a given specimen of a particular foodstuff, or more generally, how long it will take to come within a given fraction of equilibrium with a prescribed external humidity, as in storage. Conditioning times can be calculated for standard geometric shapes such as plane sheets, cylinders and spheres, if the dependence of the diffusion coefficient on moisture content is known. Such calculations may appear laborious, but, certainly with the advent of high-speed automatic computing machines, the calculations are probably a good deal quicker and cheaper than extensive measurements on large samples. Alternatively, if conditioning times are measured on small samples, the mathematical analysis shows that even when the diffusion coefficient is moisture-dependent, conditioning times for other samples of the same shape are proportional to the square of the linear dimensions.

The calculations[3, 4] show the following general properties associated with a diffusion coefficient that increases with increasing moisture content, which is what seems most often to be the case in practice:

(i) Both sorption and dehydration curves are initially linear if plotted against the square root of time, but while the sorption curve may remain linear, even beyond 50% of the final equilibrium uptake, the dehydration curve becomes concave to the (time)$^{\frac{1}{2}}$ axis much sooner.

(ii) Dehydration proceeds throughout more slowly than sorption under corresponding conditions, e.g., where sorption takes place into an initially dry specimen suspended in an atmosphere of constant humidity, and for dehydration the specimen is initially conditioned to be in equilibrium with this same humidity and is subsequently placed in an atmosphere of zero humidity.

(iii) The last stages of dehydration can be particularly slow since the last traces of moisture are removed under conditions of low concentration gradient and small diffusion coefficient.

Thus, to say that near-complete dehydration is achieved very slowly is another way of saying that the diffusion coefficient is small at low humidities.

All this is based on the assumption that the concentration at the surface of the specimen achieves equilibrium with the external atmosphere effectively instantaneously and remains constant thereafter. Numerous examples have been observed in polymer–solvent systems of sorption curves which are sigmoid when plotted against the square root of time, and of pairs of sorption and dehydration curves which intersect, dehydration being initially more rapid and finally much slower than sorption.[5] No adequate mathematical treatment of systems which behave in this way has yet been put forward, although it is generally believed that the explanation is to be found in slow changes occurring throughout the polymer structure as diffusion proceeds. In other words, the diffusion coefficient is time-dependent as well as concentration-dependent.

Some of the problems which have been investigated mathematically are of particular relevance to dehydration of foodstuffs. One or two examples are given below.

Diffusion-controlled dehydration and ' case-hardening '

It has been suggested from time to time that dehydration into an atmosphere of a certain low humidity should be faster than into a perfectly dry atmosphere. The argument is that if the diffusion within the specimen proceeds slowly at low moisture contents, a dry ' skin ' will form on the surface of a specimen in a quite dry atmosphere through which escape of further moisture is difficult. By maintaining a certain humidity in the atmosphere, it is argued, this skin can be prevented from forming and so dehydration will proceed more quickly. It has been demonstrated mathematically, however, that this is a fallacy in a purely concentration-dependent system.[6] It is particularly easy to see that the steady-state rate of transfer of moisture through a membrane can never be increased by increasing the humidity on the dry side of the membrane, other things remaining unchanged, i.e., the rate of dehydration through a membrane is always greatest into a perfectly dry atmosphere. This can be shown, too, for the rate of loss of moisture from any specimen where evaporation is controlled by internal concentration-dependent diffusion, although this is more difficult to prove mathematically. The reason for the conclusion is that the concentration distribution adjusts itself so that a low diffusion coefficient is always compensated by a high concentration gradient, but if a hard skin forms by some chemical reaction or other process and is not just a region of low moisture content, these conclusions may not hold.

Effect of a permanent skin

Many foodstuffs possess a skin having properties different from those of the underlying layers or core. The theoretical treatment of the effect that a skin may have on diffusion is here restricted to cases in which the skin and the core are each homogeneous and the boundary between the two is sharply defined. In the skin, it will be assumed that the diffusion coefficient is zero at low concentrations rising abruptly to a constant value at high concentrations as in Fig. 1 inset (a). Beneath the skin, the diffusion coefficient is assumed to be infinite. These are extreme conditions which indicate the sort of behaviour to which practical systems may tend. The calculated sorption and dehydration curves are shown in Fig. 1. Inset (b) shows a typical concentration distribution in the skin for the assumed diffusion coefficient. When the sharp front reaches the inner boundary of the skin, there is almost steady-state transfer of moisture through the skin from outside to the inner core. This persists until the inner concentration is such that the diffusion coefficient ceases to be zero in the skin, and gives rise to the linear portion of the uptake curve plotted against time. Normally this curve would be parabolic. No such linear part occurs in the desorption curve which approaches an equilibrium value consistent with the fact that the moisture content can never fall below the value at which the diffusion coefficient becomes zero. It is, in fact, the extreme case of slow dehydration in the final stage.

The effect of a skin on the uptake of moisture by a substance consisting of cylindrical fibres has been calculated for a less extreme concentration-dependent diffusion coefficient.[7] The thickness of the skin was about 1/10 the radius of the cylinder and the diffusion coefficient in the skin ranged from that in the core to 1/30 of this value. The uptake curve for a composite cylinder was found by calculation to be almost the same as that for a corresponding

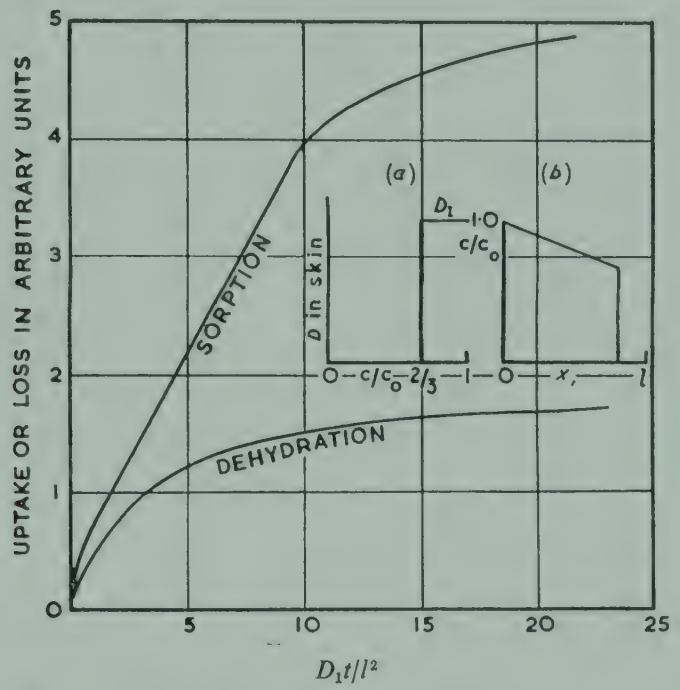

FIG. 1. *Sorption and dehydration curves for a sheet of thickness* 10 l, *having a skin of thickness* 1 *on each surface*
Here C denotes concentration, C_0 its value on the surface and x is distance measured through the skin

homogeneous cylinder having throughout the properties of the skin, except that the final stages proceeded somewhat more quickly because of the higher diffusivity in the core. The calculations further showed that the presence of a skin does not necessarily lead to a sigmoid uptake curve when plotted against (time)$^{\frac{1}{2}}$, although this has sometimes been suggested and indeed would be true for the more extreme case considered above.

Diffusion in porous solids

'Porous' in the present connexion has the meaning 'permeated by a system of interconnecting pores', examples being dehydrated fish and a mass of grain. In general, moisture can be transported through the air-filled pores and also through the solid, and at the same time there can be local transfer from pore to solid and vice versa, e.g., between a single grain of wheat and the air immediately surrounding it. The mathematics required to handle this problem depends largely on the relative speeds of the local exchange and diffusion through the solid and air-filled pores. It is assumed, as is usual in these systems, that diffusion along the solid is negligibly slow compared with that along the pores.

(i) *Rapid local exchange*

If the local exchange takes place rapidly, it can be assumed that a single grain, for example, is always in equilibrium with its immediate surroundings. Thus, if s is the total concentration of moisture in any element of volume and c the concentration in the pores,

$$s = \mathrm{f}(c) \qquad \ldots\ldots (1)$$

where the nature of the function f depends on the particular system concerned. Proceeding as in the standard derivation of Fick's second law, i.e., by equating the difference between the amounts of moisture diffusing in and out through opposite faces of an element of volume to the change of total moisture content of the volume, it is shown that

$$\frac{\partial s}{\partial t} = \frac{\partial}{\partial x}\left(D_0 \frac{\partial c}{\partial x}\right) = \frac{\partial}{\partial x}\left(D_0 \frac{\mathrm{d}c}{\mathrm{d}s}\cdot\frac{\partial s}{\partial x}\right) \qquad \ldots\ldots (2)$$

where D_0 relates to diffusion along the pores. It is then obvious that this is the usual equation for a diffusion process alone governed by a concentration-dependent diffusion coefficient D where

$$D = D_0\, \mathrm{d}c/\mathrm{d}s \qquad \ldots\ldots (3)$$

In more familiar nomenclature, the pore concentration c can be identified as a measure of the

relative humidity and so ds/dc is a measure of the gradient of the sorption or dehydration isotherm as the case may be. Thus, given a linear isotherm, s is directly proportional to c, i.e., $s = kc$, and $D = D_0/k$ and is simply reduced in the ratio k : 1. If, however, the isotherm is sigmoid and ds/dc is small at low moisture contents, then the diffusion coefficient is large. But if the isotherm obeys a power law and is steepest at low humidities, then ds/dc is large there and the diffusion coefficient is small. Dehydration isotherms of this latter shape have been observed in wheat,[8] and this then is one factor apart from any others which contributes to very slow dehydration in the final stages. A point of general interest is that a process of diffusion along pores accompanied by *rapid* local exchange with the solid walls of the pores is indistinguishable from a concentration-dependent diffusion process alone, in so far as both total uptake or loss and distribution of moisture are concerned. They only become distinguishable if the concentrations in the pore and solid are separately observable.

(ii) *Slow local exchange*

As has already been said, using wheat as an example, there are two aspects of dehydration to be considered; first, there is diffusion of moisture from the kernel of each individual grain to its surface and, secondly, there is diffusion along the pores to the external atmosphere. It may be true in general, and certainly is quite likely to be true in the final stages of dehydration, that the diffusion within a single grain is the slower process. This could, in fact, be another factor contributing to the difficulty of removing final degrees of moisture. A double diffusion process of this nature does not appear to have been examined thoroughly: the usual approximation made is that moisture enters a grain from the pore at a rate proportional to the concentration in the pore and leaves the grain at a rate proportional to the concentration in the grain. Various approximations of this kind have been examined by Glueckauf[9] in relation to theories of chromatography.

A mathematically convenient expression is

$$\frac{\partial s^1}{\partial t} = \lambda c - \mu s^1 \qquad (4$$

for the net rate of change of concentration s^1 in the grain. Here c is the concentration in the pore, λ and μ are constants. Mathematical solutions have been obtained[1] and some are available in tabular and graphical form for several values of the parameters involved. Fig. 2 shows a typical set of sorption curves, and a set of dehydration curves would be similar, for different relative speeds of pore diffusion and grain penetration. The curves cover the range from a very, very slow grain penetration leading essentially to a depressed equilibrium uptake corresponding to the amount of moisture in the pores alone, to a very fast uptake by a single grain, for which

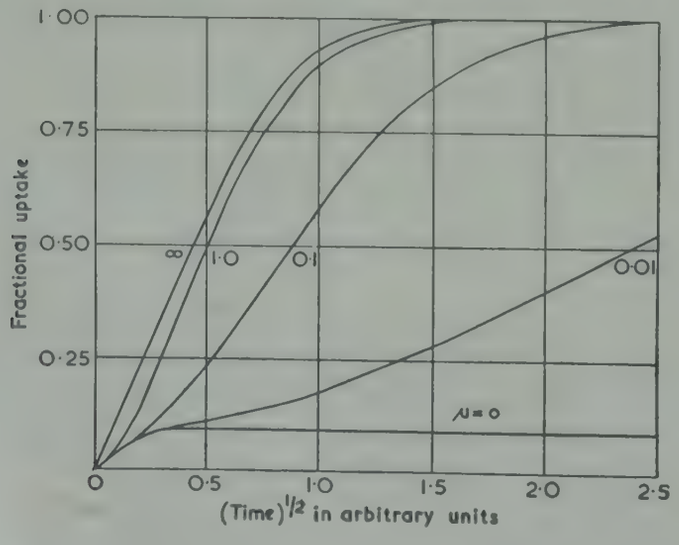

FIG. 2. *Uptake curves for a plane sheet of thickness* 2 a *with local exchange occurring according to expression* (4)
Here $\lambda/\mu = 10$, and the values of $\mu a^2/D$ are shown on the curves; the diffusion coefficient D relates to diffusion along the pores

the joint process resembles a diffusion process alone. Between these extremes, the different uptake curves are shown. The details of a diagram such as Fig. 2 differ, of course, according to what law of local exchange is assumed, expression (4) being only one example. The general features of the diagram will remain the same, however. Certain aspects of the problem of convection along pores accompanied by diffusion through the solid and also local exchange, similar to those discussed above, have been considered by Frisch recently.[10]

Simultaneous diffusion of heat and moisture

A further complication which may well arise in the dehydration of certain foodstuffs is that changes of moisture content may be accompanied by a considerable evolution or absorption of heat. This heat will itself diffuse through the medium and will affect the extent to which moisture can be absorbed. Thus we have two processes, the transfer of moisture and the transfer of heat, which are coupled together, and cannot in general be considered separately. This is too big a mathematical problem to discuss here; suffice it to say that Henry[11] has developed a very full treatment for the uptake or loss of moisture by a bale of cotton. He has given basic mathematical equations and presented results in the form of tables and nomograms. A somewhat condensed version is to be found in reference [1]. His treatment, though not his detailed results, apply to other systems of a similar nature.

Acknowledgment

The author is grateful to Mr. K. Schlacter for drawing the two diagrams.

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Discussion

Prof. Sprenger: I should like to remark that the question of diffusion while the pores change their dimensions has been treated as well theoretically as experimentally in a very thorough way by Prof. Ferraghi in his book on soil mechanics (*Erdbaumechanik auf bodenphysikalischer Grundlage*).

He found that the equations for clay under pressure are exactly the same as those for evaporation by airflow.

Dr. Crank: I was not aware of this work by Prof. Ferraghi and I am grateful to Prof. Sprenger for drawing my attention to it. I have not yet had an opportunity of seeing the book so I am not able to comment on its suitability for foodstuffs. Certainly such a change of pore diameter could be included in the variation of the diffusion coefficient though I have not myself attempted to do this.

Prof. J. Kuprianoff: In the shrinkage of solid porous foods during dehydration, a change of capillary and pore diameters is to be expected; this will very probably affect the coefficient of diffusion. Has this been covered by the assumption that diffusion coefficient is not constant or been taken into consideration in some other way?

PHYSICAL PHENOMENA DURING THE DRYING OF FOODSTUFFS

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Introduction

It is well known that imperfect control of the dehydration process for food may seriously impair the quality of the products by causing undesirable changes in shape or structure, cracks, case hardening, denaturation of proteins, browning reactions, oxidation of unstable components, or microbiological spoilage due to physical, chemical or biological processes. The drying temperature is an important factor, although heat damage is a function of both temperature and time. High drying rates in the majority of cases give rise to considerable moisture gradients within the product, which on their part cause shrinking stresses leading to crazing and cracking with sensitive products. It may be important to know whether evaporation takes place in the surface layer or more inside the product, because liquids migrating to the surface sometimes carry solutes which tend to seal the product and cause case hardening.

Full insight into the complex phenomena of the drying process has so far not yet been gained. Apart from the direct influence of the deprivation of moisture, there must be considered effects caused by the fundamental processes of heat transfer, flow of liquids and vapours, and the chemical changes wrought by the drying gas. Further research into the fundamental processes going on during drying and a study of the physical properties of the product will lead to proper control of the secondary processes so important for quality and to the establishment of a procedure for a rapid but gentle dehydration.

Laws governing the fundamental processes

Heat transfer

Heat transfer occurs at points where a temperature gradient exists, i.e., between the evaporating substance and the heat carrier. Heat transfer within the product is governed by the well-known laws of heat conduction. The heat conductivity, λ, is dependent on both temperature and moisture, although in most cases it is sufficient to know the heat conductivity of the dry part of the product. The heat conductivity of moist, porous substances may be evaluated by considering the water vapour diffusion in the pores.[1] The individual properties of the product play no part in the heat transfer from the drying air to the substance as long as its surface has a moisture content such that one can assume a uniform saturated water vapour pressure over the entire surface at the temperature of the product. The fact that there exists a known relation between the heat transfer coefficient, α, and the material transfer coefficient, β, dependent on the state of movement, permits the calculation of the surface temperature of the moist product. Recent investigations[2] have shown that the surface temperature of a moist substance differs only slightly from the temperature of the wet-bulb thermometer. This only holds when the evaporation effectively takes place at the really moist surface.

Movement of moisture

According to our present knowledge the following kinds of movements of moisture may occur in the product during the drying process:

Liquid movement caused by capillary forces.—As a unique relation exists between the capillary tension and the moisture content,

$$W_w = -A\ kX.\frac{dX}{ds} \qquad \text{(1)}$$

where W_w = weight of water subjected to capillary movement
A = cross-sectional area of product
kX = liquid conductivity
X = moisture content of product
s = thickness of product

The liquid conductivity kX is dependent on the capillary distribution and its value varies greatly with the moisture content.

Diffusion of liquids caused by differences in the concentration

$$W_w = A\delta_c.\frac{dc}{ds} \qquad \text{(2)}$$

where δ_c = the diffusion coefficient dependent on the concentration
c = concentration

Surface diffusion in liquid layers adsorbed at the boundary of solid substances:

$$W_w = -U \cdot \delta_b \cdot \frac{dc_b}{ds} \quad \ldots\ldots (3)$$

where U = circumference of pores
δ_b = surface diffusion coefficient, dependent on the concentration
c_b = surface concentration

Water vapour diffusion in air-filled pores caused by differential partial pressures.

Where the pore diameters are larger than the mean free path of the water vapour molecules, the diffusion may be computed by Stefan's law.[3] Its application to the water vapour diffusion in products undergoing drying is made possible by the introduction of the diffusion-resistance factor μ as suggested by Krischer:[4]

$$W_v = -\frac{A}{\mu} \cdot \frac{\delta}{R_v T} \cdot \frac{P}{P-P_v} \cdot \frac{dP_v}{ds} \quad \ldots\ldots (4)$$

where δ = diffusion coefficient of water vapour in air
R_v = gas constant of water vapour
T = absolute temperature
P = total pressure
P_v = partial pressure of water vapour

The diffusion resistance factor, μ, is defined as the number of times the resistance in the product is higher than in an equally thick stationary air layer. Since μ varies reciprocally with the free pore area of the product available for the diffusion process and is also a measure of the detours the water vapour molecules have to follow, it is best to subdivide μ into an area factor and a path or distance factor. Thus it is possible to evaluate μ by way of the free pore volume and the structure of the product.[5] The Stefan diffusion being directly proportional to the total pressure but inversely proportional to the partial pressure of the air, it is possible to hasten the dehydration of products with sufficiently large effective pore diameters by evacuation.

In pores where the diameter is smaller than the mean free path of the water vapour molecules, there is molecular or Knudsen flow. Because this flow is not influenced by the partial pressure of the air, it is not possible to speed up the dehydration of products with such pore diameters.

Vapour flow causes differences in the pressure in dehydration processes where the heat transfer occurs in a special way or when dehydration is effected in a vacuum at the boiling point of the liquid present. With pore diameters exceeding the mean free path of the vapour molecules, the flow obeys Poiseuille's equation.

It is possible to explain the course of the drying process by the aid of equations for the individual processes and it is further possible to determine certain physical properties which are responsible for the drying behaviour of the products. With this knowledge the course of the dehydration can be predicted under any ambient conditions for some characteristic points where only one or only a few of the properties which play a part in the dehydration process are of importance. Although an exact prediction of the entire drying curve cannot be made on account of the extremely complex nature of the process and the dependence of the properties on moisture, it is nevertheless possible to control the process qualitatively and quantitatively in its more important aspects.

The behaviour of vegetable substance during dehydration

Vegetable products are hygroscopic and therefore the water vapour pressure above the liquid of the product is not only dependent—as in the case of free water—on temperature, but also on the moisture content. Hygroscopic substances, during drying, tend towards a residual moisture content at which the vapour pressure of the adsorbed moisture is equal to the water vapour pressure of the surroundings. The state of equilibrium between the moisture of the product and the water vapour pressure or the relative humidity (R.H.) is described by the sorption isotherms. Fig. 1 shows some sorption isotherms for potatoes measured by the author. Below a certain moisture content, which, for example is 1·2 kg. kg. at 20° in this instance,

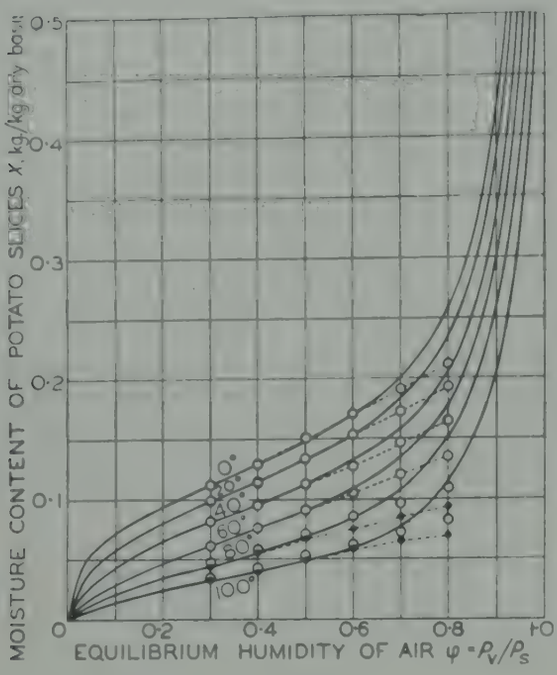

FIG. 1. *Sorption isotherms of potatoes at different temperatures*

Full curve: experimental values. Broken curve: calculated after Brunauer, Emmett & Teller[6] for 4 (●) and 5 (○) adsorbed molecular layers. P_V equilibrium vapour pressure, P_S pressure of the saturated vapour at the test temperature

the water vapour pressure decreases steadily with decreasing moisture content. Thus it is only possible, when drying in an air current at 40° and 13% R.H., to achieve a final moisture content of 5%.

From the sorption isotherms[6] it is possible to obtain an idea of the characteristic pore sizes of the product and of the binding energy of the adsorbed moisture. An evaluation of the 20° sorption isotherm, following the theory of Brunauer, Emmett and Teller for polymolecular adsorption showed, for instance, that up to 7·7% moisture there is monomolecular adsorption at the inner surface, and up to 15% moisture, an adsorption by capillary condensation at the minute pore menisci of the substance. Taking the diameter of the water molecule as 2 Å, a value of 10 Å is obtained for the maximum thickness of the adsorption layers. Using Kelvin's formula for the lowering of the water vapour pressure in the transition range to capillary condensation gives a capillary radius of 11 Å with potato juice as liquid medium. Although these values are only of theoretical interest, they nevertheless give a good idea of the pore volume of the product. The latent energy which must be furnished, in addition to the evaporation energy during the evaporation of the adsorbed moisture, was determined at about 1430 B.Th.U./kg. with the lowest moisture contents. The latent energy decreases rapidly in the range of polymolecular adsorption and is negligible for capillary condensation.

Fig. 2 shows the drying curve of a potato slice for one-sided drying with relative moisture X_m/X_o with the average moisture content at any given time divided by the initial moisture content as abscissa and the product of drying rate and sample thickness (taking account of the shrinking) as ordinate. The shape of the curve shows that there are two breaks between the three parts of the curve (convex towards the abscissa), separating the three stages

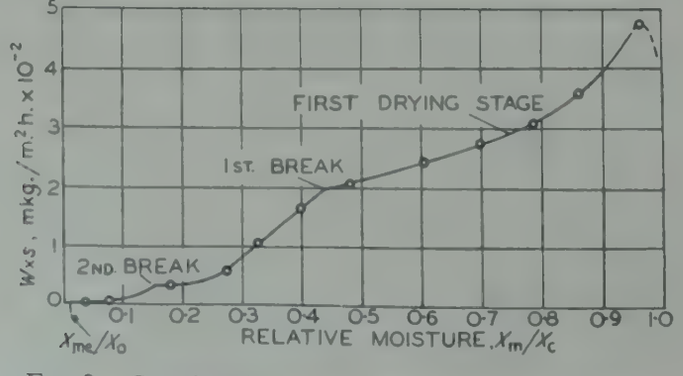

FIG. 2. *Complete drying-rate curve for one-side drying of potato slices in an air current at 60°*

of the drying process. Systematic drying tests[6] made with cylindrical potato slices of different thicknesses show that the breaks for samples dried at the same temperature lie on a well-defined curve (Fig. 3). The fact that such break curves (lines joining the break at the end of the first drying stage during which moisture movement occurs only in the liquid state) exist has already been theoretically deduced for non-hygroscopic substances.[7] A further result of the tests was the fact that the distances along the ordinate between the break curves for different temperatures of the substance vary as predicted by the theory according to the change in the ratio of surface tension to the viscosity of the liquid of the product due to the temperature variation. From this it may be concluded that with vegetable products, the moisture transfer during the first drying stage takes place only by means of capillary movement towards the surface. The rate of drying is nevertheless not constant. It decreases owing to the deformation of the surface caused by shrinkage. Accordingly, the temperature within the product does not remain constant during the first drying stage, but it rises continually to a value at the first break which is considerably higher than the wet-bulb temperature. During the second drying stage, the evaporation goes on in the interior of the samples. The second break appears when no part of the sample has a moisture content exceeding that of the hygroscopic range. For the mean moisture content, X_m, at the second break,

$$X_m = \tfrac{1}{2}(X_{hygr.max.} - X_e) \qquad (5)$$

where $X_{hygr.max.}$ = the maximum hygroscopic moisture content of the substance

X_e = the equilibrium moisture content.

In the third drying stage all the inner portions of the sample are involved in the drying. As the vapour pressure within the product, which is responsible for the diffusion in the interior of the product, decreases with the decreasing moisture content and as the diffusion resistance

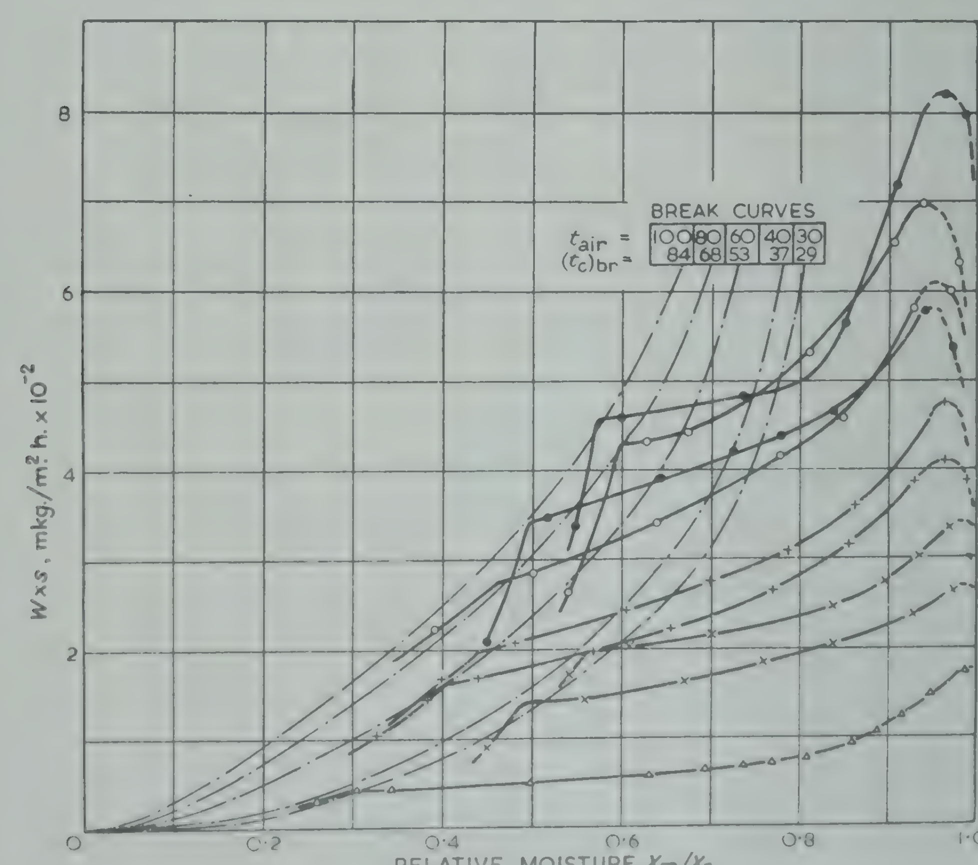

FIG. 3. *Drying-rate curves for the first drying stage and break curves for one-side drying of potato slices in air currents of varying temperatures*

$(t_c)_{br}$ temperature of the sample at the break-point

t_{air} Δ 30° × 40° + 60° ○ 80° ● 100°

factor, μ, increases on account of the shrinkage, the drying rate is continuously reduced until it vanishes when the equilibrium moisture is reached.

In addition to the sorption isotherms and the break curves, further physical properties of the product characteristic for the drying process were found, i.e., the liquid conductivity, k_x, and the diffusion-resistance factor, μ, both of which are related to the moisture content. They were computed by determining the moisture distributions occurring within the samples after different drying times and by means of special diffusion experiments. The liquid conductivity is rather high at the beginning of the drying process and tends to zero for the lowest moisture contents. At the maximum hygroscopic moisture content, when the system of fine capillaries becomes effective, there is a maximum of k_x. According to the theory of capillary movement, this is always the case when the number of capillaries changes abruptly. Two curves were found for the diffusion resistance factor: the lower one for samples whose temperature did not exceed 60° during the whole drying process and the upper one for such samples whose temperature exceeded 60° before the first break was reached. The curves show an extraordinarily steep increase of μ with decreasing moisture content which is due to the reduction of the pore diameter caused by the shrinking and by the serious influence of the temperature, which evidently brought about a case hardening (Fig. 4).

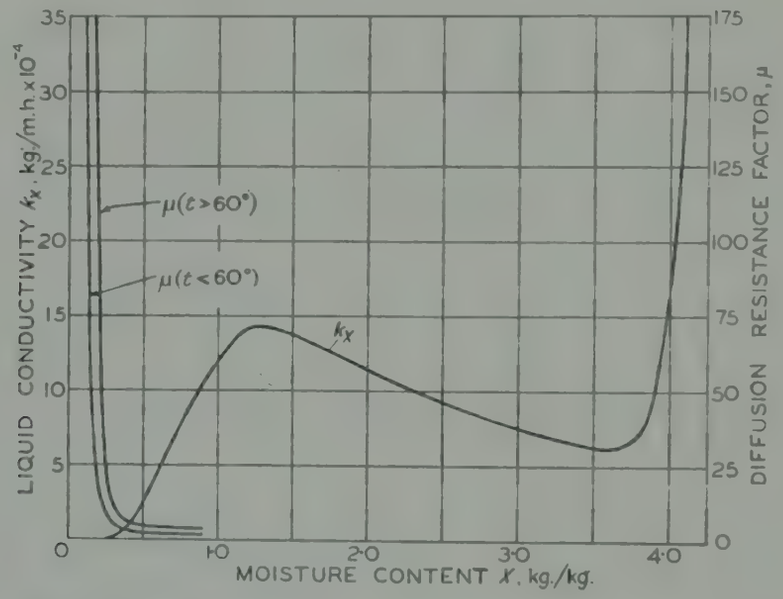

FIG. 4. *Liquid conductivity,* k_x, *and diffusion resistance factor,* μ, *as a function of the moisture content,* X, *in one-side drying of potato slices*

Not only are the above pointers furnished by such an analysis of the fundamental physical processes and the determination of those physical properties important for the drying process, but valuable information is obtained as to how to prevent undesirable processes leading to impairment of quality.

An approximate prediction of the physical behaviour during dehydration and of the drying times for any drying conditions can be made as soon as the following data of the product to be dried are known:

(1) Sorption isotherms; (2) Break curves; (3) Effective pore diameter; (4) Diffusion resistance factor; (5) Heat conductivity.

Unfortunately these physical properties have been determined completely for only a very few foodstuffs. We also lack exact information on moisture movement in bodies where only movement of liquids is possible and which shrink heavily during drying. Among these may be mentioned wheat preparations such as spaghetti, vermicelli, macaroni and noodles which tend to crack either during or after dehydration owing to high shrinkage stresses. An exact prediction of the magnitude of the mechanical stresses for any given drying conditions, with the aid of all pertinent physical properties of the product, is therefore not yet possible. During an extensive research on the occurrence of stresses in the drying of macaroni made by Beuschel[8] at this

Institute it was found that, as soon as the physical properties of the product responsible for the formation of stresses are known, a few simple measurements during the drying process suffice to determine stresses dangerous for the product.

Determination of shrinkage stresses during the drying of macaroni

By analogy with the definition of the coefficient of thermal expansion, the linear shrinkage with uniform moisture distribution has been characterized by the coefficient of linear shrinkage:[9,10]

$$\alpha = \frac{1}{l_0} \cdot \frac{\Delta l}{\Delta X} \qquad (6)$$

where l_0 = initial length

Δl = constriction

ΔX = differential moisture content.

As long as this relation holds, the shrinkage is called ' unrestrained ' or ' free.' Where additional forces caused by adherence or friction are active, the shrinking is restrained. Which kind of shrinking takes place during the drying of macaroni? Since the moisture movement occurs in the liquid stage, moisture gradients appear in the product, which, according to equation (1), must increase with the drying rate. The parts closer to the surface dry more quickly, so that the tendency to shrink is higher in the outer layers. But the shrinkage of these outer layers is restrained by the adjacent layers due to inner friction. Thus shearing stresses appear along layers parallel to the surface, whereas at right angles to the surface there is either compressive or tensile stress.

The response of dough to mechanical stresses is dependent to a great extent on the moisture content. Fig. 5 shows stress–elongation curves of macaroni dough of different moisture contents. At high moisture contents stresses cause purely plastic deformations, while at lower moisture contents elastic properties play a role and the tensile strength of the dough increases. In Fig. 6 Young's modulus, E, obtained from the stress–elongation curves, and the tensile strength, σ_z, are plotted against the moisture content X. In the plastic stage, tensile stresses are reduced by plastic deformation, whereas in the elastic stage they cause an elastic deformation. The two stages are, however, not sharply defined.

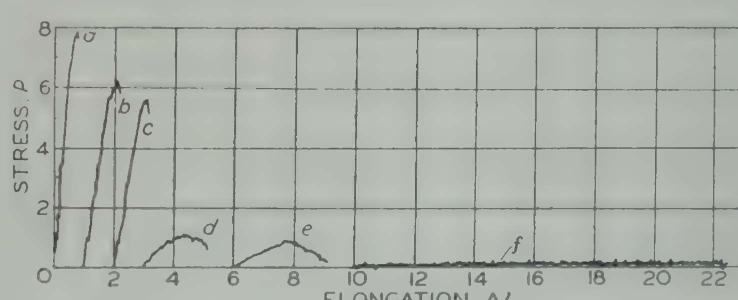

FIG. 5. *Stress–elongation curves of macaroni dough for different moisture contents*, X
(arbitrary units)

	a	b	c	d	e	f
X (kg./kg.)	0·154	0·170	0·180	0·255	0·279	0·365

With restrained shrinking the observable effective relative shrinkage, e_{real}, which is actual shrinkage, Δl_{real}, divided by initial length, l_o, is composed of two parts: of the theoretical free shrinkage $e_{theor} = \Delta l_{theor}/l_o$ due to the moisture loss $\Delta X = X_o - X$, and the deformation Δe caused by the shrinkage stresses P:

$$e_{real} = e_{theor} - \Delta e \qquad (7)$$

The theoretical relative shrinkage may be obtained from equation (8):

$$e_{theor} = \alpha(X_o - X)/l_o \qquad (8)$$

For the plastic–elastic deformation caused by the shrinkage stresses

$$\Delta e = \Delta e_{plast} + \Delta e_{elast} = \frac{P}{E} + \int \frac{P}{\eta}\, dt \qquad (9)$$

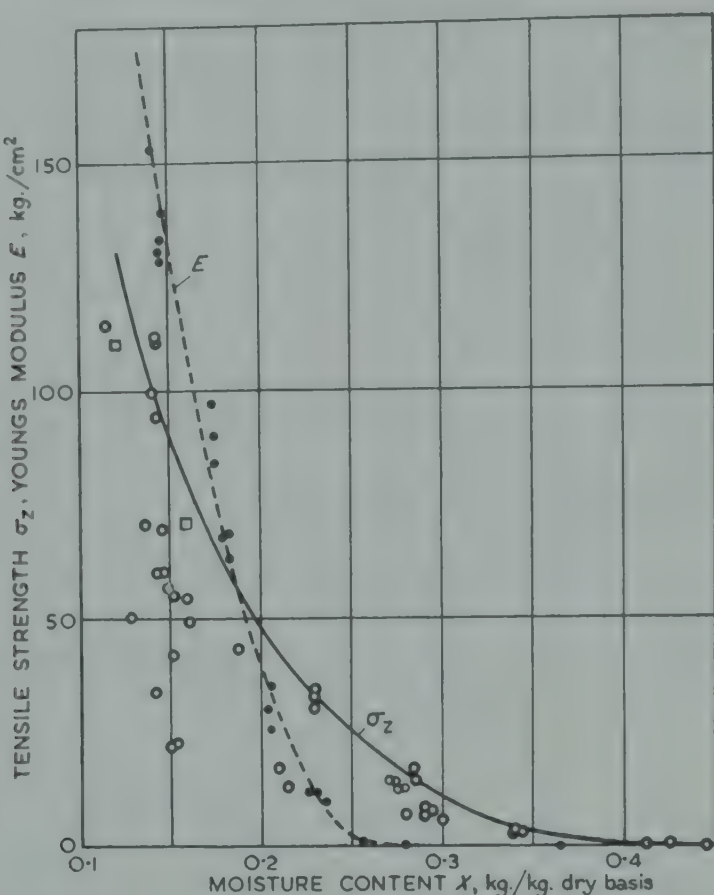

FIG. 6. *Dependence of tensile strength, σ_z, and Young's modulus,* E, *of macaroni dough on its moisture content,* X

□ σ_z after Earle & Ceaglske[9]

where Δe_{plast} = plastic deformation

Δe_{elast} = elastic deformation

E = Young's modulus
η = coefficient of viscosity } both dependent on X

As it is not possible to determine both deformation components individually, it is assumed that above the so-called critical moisture, X_c, only plastic deformations appear and if $X < X_c$ only elastic deformation takes place. It is convenient to choose X_c as the centre of the transition from the plastic to the elastic stage. According to the findings of Earle & Ceagslke[9] and tests made at this Institute, the critical moisture content of macaroni dough may be put at $X_c = 0{\cdot}28$ kg./kg. Assuming that all shrinkage stresses vanish in the plastic stage and that for moistures below the critical value only elastic deformations occur, only the plastic deformation Δe_c at the critical moisture X_c need to be taken into account in order to obtain the stresses in the elastic range. Thus the elastic deformation component can be obtained from equations (7–9):

$$\Delta e_{elast} = \alpha(X_o - X) \, . \, l_o - e_{real} - \Delta e_c \quad \text{(10)}$$

and the shrinkage stress

$$P = E \, . \, \Delta e_{elast} \quad \text{(11)}$$

Fig. 7 shows the relation between the moisture distribution, shrinkage and shrinkage stresses at a mean moisture content for single-face drying.

When the uniform initial moisture, X_o, has been reduced to an average moisture content, X_m, the moisture within the product decreases from the bottom towards the surface according to the curve $X = f(s)$. At a distance s_1 from the surface, the critical moisture X_c obtains. The theoretical shrinkage, which can be computed according to equation (8) from the moisture loss in the different layers, corresponds to the broken curve e_{theor}, whereas the observable shrinkage

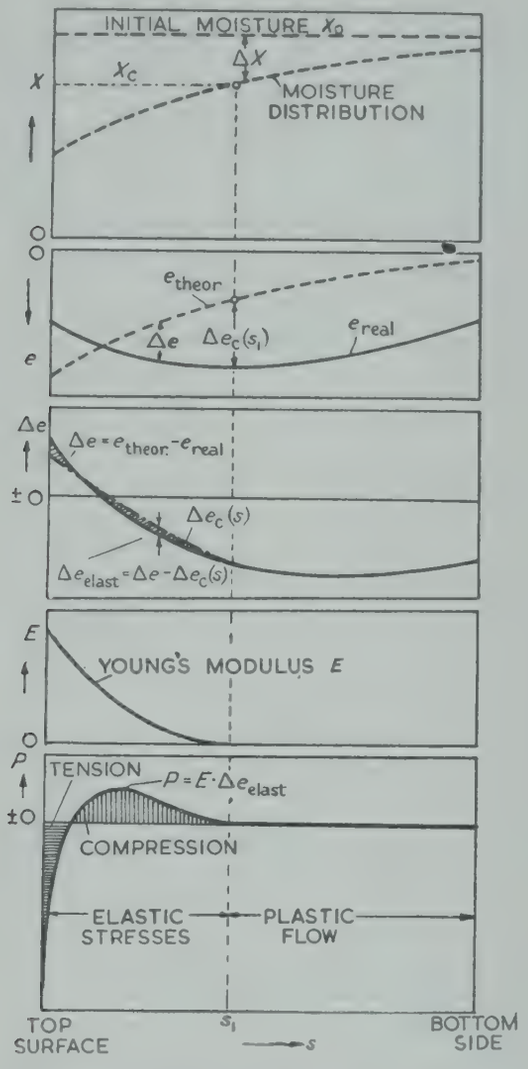

FIG. 7. *Relation between the moisture distribution, shrinkage and shrinkage stresses at a mean moisture,* X_m

is represented by the full curve e_{real}. The deformation Δe caused by the shrinkage stresses is given by the difference between the two curves. For depths $s > s_1$ beneath the surface, the deformation is purely plastic. For depths less than s_1 the total deformation, Δe, is composed, according to equation (9), of the plastic deformation, $\Delta e_c(s)$, which obtained at the depth s with the critical moisture X_c and of the elastic deformation Δe_{elast}. Equation (11) requires that this elastic deformation has to be multiplied by Young's modulus valid for the moisture content X in order to get the momentary shrinking stress at depths $s < s_1$. Fig. 7, which is only a diagrammatic sketch, shows that there are tensile stresses in the top layers and compressive stresses in the middle layers. In depths below s_1 all shrinkage stresses have been reduced to zero by plastic flow.

Only in the regions of tensile stress is there any danger of crazing or cracking. Since the highest tensile stresses occur only in the driest parts of the piece, it suffices to investigate merely its surface. At convenient intervals during the drying process the observable shrinkage, e_{real}, as well as the instantaneous moisture content of the surface must be measured. From these values the theoretical shrinkage, e_{theor}, must then be calculated using equation (8) for the different moisture contents. From the plotted curves e_{real} and e_{theor}, the deformation Δe_c at the critical moisture content, X_c, which is assumed to be solely plastic, can be obtained as the difference of their ordinates. The next step is to calculate from equation (10) the elastic deformation, Δe_{elast}, in the range below the critical moisture where the deformation is assumed to be purely elastic. Finally the value of Δe_{elast} multiplied by the corresponding Young's modulus E valid for the moisture content of the surface layer, leads to the instantaneous shrinkage stress in this same layer as proved by equation (11).

To simplify the calculation, a working diagram (Fig. 8) was developed following a suggestion of Barkas.[11] Along the abscissa are plotted the deformation, e, and the moisture content, X, related to each other by equation (8) at vanishing stress P, and along the ordinate the tensile stress P. Also included are stress–elongation curves at different moisture contents starting from the corresponding moisture content on the X scale. The tensile strength corresponding to any moisture content is marked on the corresponding P, e curves. The origin of the scale for the deformation lies at the critical moisture X_c. The region of plastic deformation lies to its right, that of elastic deformation to its left.

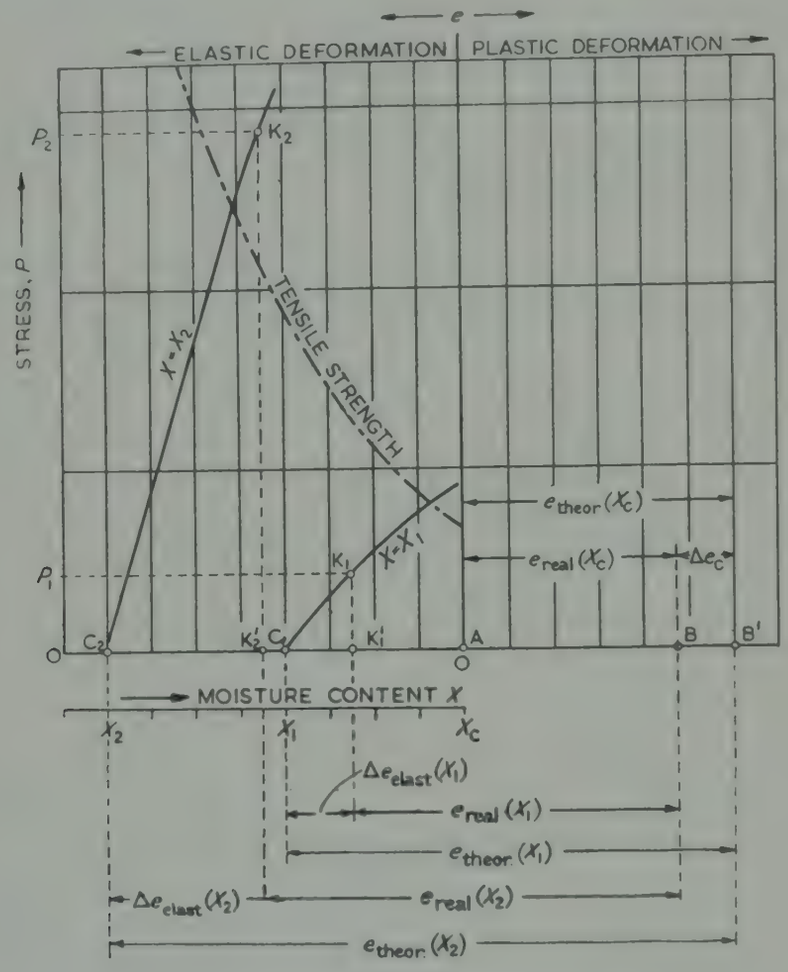

FIG. 8. *Construction of stress diagram*

In order to apply the diagram to a given drying procedure it is necessary to plot along the abscissa from the origin to the right both the theoretical shrinkage, e_{theor} (X_c) (length A–B′), and the observable shrinkage, e_{real} (X_c) (length A–B), obtaining at the time the critical moisture, X_c, is reached in the surface layer. The shrinkage values, e_{theor} (X) and e_{real} (X), for lower moisture contents of the surface layer are then plotted to the left starting from the points B′ and B respectively and scaled off as lengths $B'C_1$ and BK'_1 respectively. The resulting length $C_1K'_1$ is then equal to the elastic component of the deformation, Δe_{elast} (X_1), which, in its turn, is responsible for the stress P_1 at moisture content X_1 in the surface layer, as shown by equation (11). The stress P_1 can therefore be found on the stress–elongation curve belonging to a moisture content X_1 in a point K_1 directly above K'_1. In cases where, as exemplified by the sample with moisture content X_2, the resulting stress exceeds the tensile strength, crazing or cracking is liable to occur.

Experimental determination of the mechanical stresses

To obtain a complete stress diagram for macaroni dough, not only must the stress–elongation curves and the values of the tensile strength (Fig. 6) be obtained, but also the coefficient of shrinkage, α. For this purpose a thin cylindrical sample was inscribed with two parallel lines

and their variation in distance observed under a microscope during very slow drying in a hygrostat. α was found to be on the average 0·3 and was practically independent of the moisture content. The curves of the stress diagram of Fig. 9 show the stress changes with three different procedures for the drying of macaroni. Test A corresponded to the current practice of the macaroni producers, in which, during 26 hours of drying, the air temperature is raised slowly from 25 to 42° and the R.H. is lowered slowly from 87 to 80% during the first 12 hours and then rapidly. On account of the high humidity of the air, the surface moisture decreases only slowly, so that the non-vanishing stresses appear comparatively late, but they increase continuously and are maximum at the end of the drying process with a value just below the tensile limit. The product therefore tends to crack after leaving the dryer.

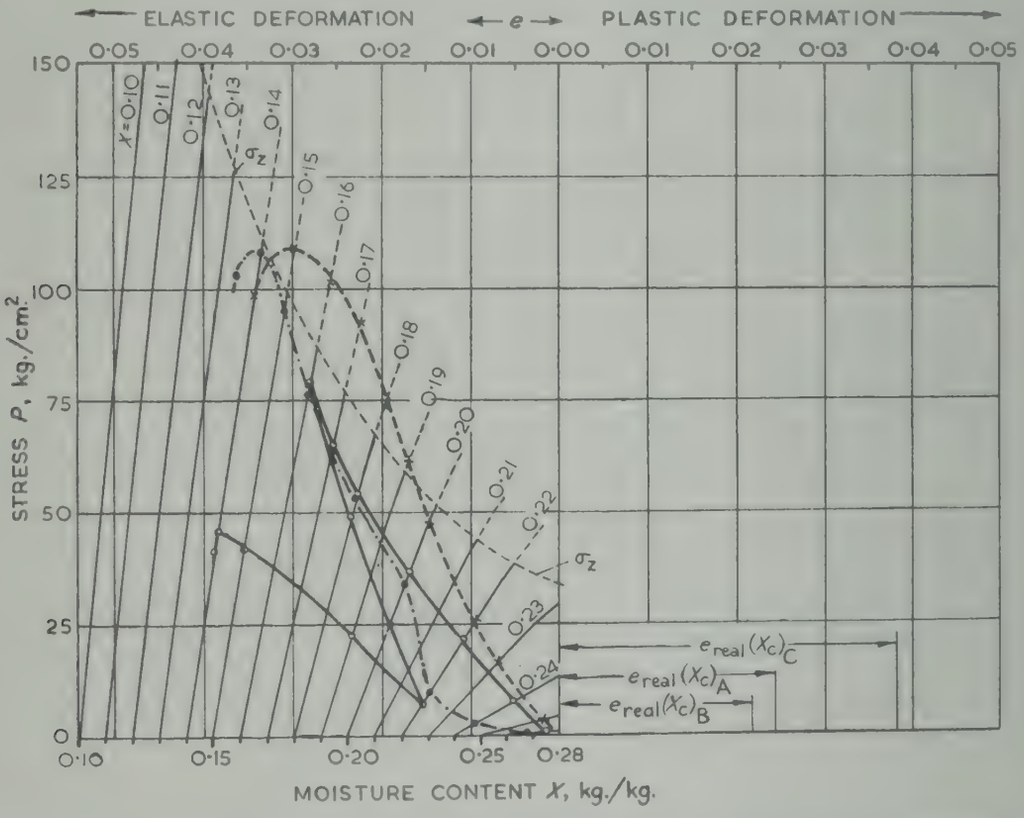

FIG. 9. *Diagram for the determination of shrinking stresses,* P, *in the surface of macaroni for a given moisture content,* X

The fan-shaped curves inclining towards the right are stress–elongation curves for different moisture contents. A, B, C stress curves for different drying procedures. $e_{real}\ (X_c)_{A,B,C}$ = observed deformation at $X = 0{\cdot}28$ kg./kg. (beginning of elastic deformation)

·—·—·—· Test A
– – – – – – – – Test B
———— Test C

In test B the first drying was accelerated by raising the air temperature to 70° during the first hours with the R.H. at 90%. Thereafter the temperature was lowered to 40° and finally to 30°. In order to reduce the high moisture gradient formed within the product during the first phase, the drying was interrupted for a short time after the second hour by raising the R.H. to 97% and then it was consistently lowered. The stress diagram shows that the reduction of the moisture gradient was made too early and that the drying after the sweating period was too forced, therefore the stresses quickly passed the tensile limit. In addition, the high temperatures caused undesired changes in the product.

Based on the results of both previous tests, a further test, C, was made with 60° as starting temperature. The R.H. was fixed at 52% at the start to reduce the average moisture content as rapidly as possible, but to reduce the moisture gradient and the stresses built up in the top layers during the first stage, the R.H. was raised to 95% within the first 3 hours and the temperature lowered after 2 hours. Fig. 9 shows that the stresses were effectively lowered after their building up to a maximum. The mean moisture content of the product having been

considerably lowered by the first rapid drying period, the final drying after the rewetting of the surface for the purpose of reducing the steep moisture gradient was performed under the drying conditions of test B without any high stresses appearing. The permanent stresses at the end of the drying process were considerably lower than in the tests A and B, and therefore there was less danger of crazing. The total time of drying was reduced to 16 hours.

This investigation shows that proper analysis of the physical processes taking place in the product enable an improved control of the drying process which could not have been gained in an entirely empirical way.

Summary

To improve the quality of dehydrated foodstuffs it is essential to have a detailed knowledge of the basic physical phenomena occurring during the drying process. The laws of heat and moisture movement governing the primary processes are already well known. By their aid it is possible to determine physical properties characteristic of the drying behaviour of the foodstuffs. The drying of potato slices served as an illustration.

Although the rather complex interaction of many elementary processes and the serious dependence of the physical properties on the moisture content do not permit an accurate computation of the drying rate curve, the progress of the drying process may be predicted for all important points if the following data of the product to be dried are known:

(1) Sorption isotherms; (2) break curves; (3) effective pore diameter; (4) diffusion-resistance factor; (5) heat conductivity.

If these data are available useful recommendations for the proper control of the dehydration process may be given which also enable the prevention of undesirable secondary effects leading to deterioration of the product. Without a satisfactory insight into these secondary effects it is impossible to find a drying procedure which is time-saving and does not reduce the quality of the product.

The principles developed herein were applied to the drying of macaroni dough. An analysis of the shrinkage stresses and the determination of physical properties connected with the occurrence of such stresses made it possible to develop a procedure for the calculation of tensile stresses in the surface of the product which may mar the product by cracking or crazing either during or after drying. Using this method, a marked improvement of the procedure for the drying of macaroni was obtained.

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Discussion

Dr. B. P. Fish: Your work on stresses set up in materials on drying tempts me to comment upon the shape of dried materials. In a disc of starch gel, stresses set up by drying can be relaxed by a process of folding and shrinking. When a disc dries freely from both faces the edges dry more quickly than the central portion probably because eddies set up around these edges help the transport of moisture from the periphery. The edge remains rigid while the centre shrinks and the final product is a 'saddle'-shape or hyperbolic paraboloid (cf. some dried potato products).

Mr. C. G. Tucker interpolated that potato strips when dried had a cruciform structure.

Dr. P. B. Fish: If each face of a rectangular prism shrinks inwards to form surfaces with hyperbolic sections, the arms of the cross will be the directions of the asymptotes to the four hyperbolic surfaces.

Mr. C. G. Tucker then mentioned the ' hat '-shape of the section of dried carrot.

Dr. P. B. Fish: This must be the antithesis of my ' saddle '-shape. The medulla region in the carrot cannot shrink but folds as the outer ring dries.

Dr. A. C. Jason interpolated a remark concerning diffusion in the capillaries during drying of foodstuffs.

Dr. P. B. Fish: It is necessary to distinguish carefully between diffusion in capillaries under the ' driving force ' of a concentration or potential gradient, and movement of water from larger to smaller capillaries under the action of surface tension. These processes may have different temperature coefficients because of the effect of temperature on surface tension, which may permit an experimental distinction to be made.

Dr. P. Görling: The deformations and foldings, as mentioned by Dr. Fish and Mr. Tucker, are caused by the non-uniform decrease of moisture content in the pieces. The condition for these phenomena is a plastic flow of the material at higher moisture contents under shrinkage stresses. Should the moisture content decrease uniformly in all parts of the piece, the shrinkage would not be accompanied by deformation. On the other hand, an ideal elastic body would have the same form after drying as before in all cases.

The temperature coefficient of the moisture transport in the material can be very useful indeed in distinguishing liquid movement caused by capillary forces from diffusion of liquid, caused by differences in concentration. The capillary liquid movement is dependent on both the surface tension and the viscosity of the liquid. If curves are found joining the breaks at the end of the first drying stage, and if their distances along the ordinate are found to vary with temperature to the same extent as the ratio of surface tension to viscosity, as in the case of potatoes, it may be concluded that capillary liquid movement is the underlying mechanism during the first drying stage.

Besides, the rate of moisture movement may also suggest the nature of moisture movement, as liquid diffusion in general proceeds much more slowly than capillary liquid movement.

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SESSION III

Chairman : A. C. Jason

RATE-CONTROLLING FACTORS IN FREEZE DRYING

By H. KRAMERS

(*Laboratorium voor Physische Technologie, Technische Hogeschool, Delft, Netherlands*)

After a general discussion of the factors influencing the rate of drying, an account is given of some experimental work on the structure and the resistance to vapour flow of freeze-dried materials. Finally, some aspects of continuous freeze drying are discussed.

Introduction

In freeze drying, water is removed from a product in which the water is in a frozen state, a method which has been in use for over 50 years for the preservation of small amounts of biological substances. Drying at such low temperatures has advantages for heat-sensitive materials, and the extremely good reconstitution of freeze-dried substances is an attractive feature of this method. Application on a larger scale started about 15 years ago for the drying of blood plasma and penicillin. Because of the good quality of freeze-dried products, application to other products on a large scale has been considered during the past 10 years, but because of the high cost of this operation it is only feasible for products where the quality is of primary importance.

There has been considerable literature during the last 15 years dealing with freeze drying as a new ' engineering science,' but it is not intended in this paper to review all the literature. Rather, discussion is restricted to a consideration of the drying rate which is of interest for design purposes and ultimately as regards the cost of drying. Only a general presentation will be given of the factors governing the drying rate. The most important factor, the permeability of the dry layer, will be treated more fully on the basis of some experimental evidence.

Rate of drying

For this discussion, the usual arrangement is assumed where a layer of the frozen material is deposited on a solid carrier material through which the heat of sublimation is to be supplied. On evaporation of the ice, its surface recedes in the layer, and the water vapour has to be transported through the part of the layer which has already been dried. The vapour then passes through an evacuated space to, e.g., a surface condenser, on which an ice layer is formed as the evaporation proceeds.

In such a process, heat, either sensible or latent, is transported from a higher to a lower temperature. The relationship between the total temperature difference and the heat flow (which is proportional to the rate of evaporation) is governed by the resistances to the flow of heat.

Fig. 1 represents possible distributions of temperature and water-vapour pressure in the solid and vapour phases respectively. The various individual resistances are discussed below.

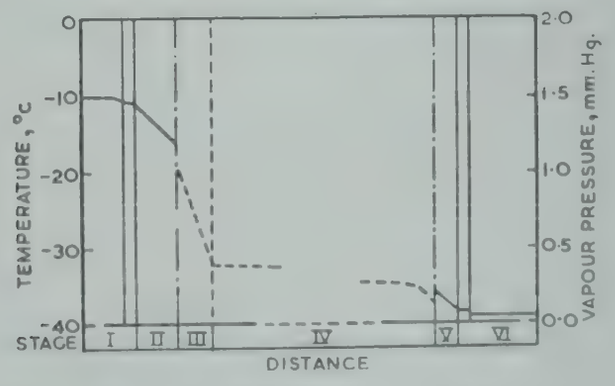

FIG. 1. *Schematic representation of temperature and pressure drops in a freeze-drying operation*

Stage I. Heating medium and wall.
II. Frozen material.
III. Dried material.
IV. Vapour space.
V. Ice on condenser.
VI. Condenser wall and cooling medium.
——— temperature. — — — — vapour pressure.

I. *Heat supply to the frozen material*

The heat may be supplied by convection of a liquid or a gas or by condensation of a vapour on the heating surface. An example of the latter case has been described by Spaander[1] who heats glass bottles containing frozen blood plasma by surrounding them with an atmosphere of warm air saturated with water vapour. The conditions should be such that the condensate does not freeze.

With these methods of convective heating, the heat has to be transported by conduction through the container wall to the frozen material. If this wall is thick (3 to 5 mm.) and if it has a low thermal conductivity (glass or plastic), the temperature drop over the wall may be of some importance; at the usual drying rates of 1–2 kg. m.^{2}/h., temperature drops of 2–10° may be expected. A good thermal contact between the wall and the frozen material has to be ensured.

Alternative ways of heating have been suggested. Zamzow & Marshall[2] have investigated the use of low-temperature radiant heating; it has the advantages that a good thermal contact between the wall and the ice is not indispensable and that the heat can be more uniformly absorbed in the frozen material, provided the wall transmits the radiation used.

In general, the supply of heat to the frozen material is not a great problem, the main technical requirement being that the temperature of the frozen substance should nowhere exceed a certain value, which may be well below the freezing point of water (e.g., because of its salt content). In this respect the convective heating methods are safer than radiant or dielectric heating.

II. *Transport of heat in the frozen material*

In the case represented in Fig. 1, the heat of sublimation has to be conducted through the frozen material to the evaporation surface. The resistance to heat flow of the frozen layer depends on its thickness and on its thermal conductivity. For pure ice the latter value is reported to be 2·4 w/m. °c, but greater values can be found for water and frozen solutions if the conductivity is measured in the same direction as the heat flow previously applied in the freezing period. Thus, for milk, which had been frozen at a rate between 0·4 and 0·8 mm./min., thermal conductivities were found[3] between 3·1 and 3·7 w/m. °c.

At drying rates from 1 to 2 kg. m.^{2}/h., the temperature gradient in the frozen layer will lie between 0·2 and 0·5 °c/mm. As the drying proceeds the temperature drop over the frozen layer will decrease in proportion to its thickness.

III. *Resistance of the dried material to water-vapour flow*

The vapour which is produced at the evaporation surface has to be transported through the dry material. This involves a pressure gradient which is roughly proportional to the drying rate and depends very much on the structure of the dried layer. It is thus very difficult to predict this resistance to vapour flow, which in practice may be complicated by inhomogeneities in the frozen solution or suspension and by structural changes during the drying process (e.g., the development of cracks). The effect of the dry layer will be treated in more detail in the next section.

In the evaporation of the ice, much attention has been given to the question of what the maximum possible evaporation rate in vacuum would be and whether this would be a rate-limiting factor in freeze drying. This maximum evaporation rate can be represented by Knudsen's formula:

$$\Phi_{max} = \alpha p \sqrt{\frac{M}{2\pi RT}}, \quad \cdots\cdots \quad (1)$$

where α is the evaporation coefficient. For ice, α is of the order of unity.[4, 5] If at this maximum rate the heat of evaporation had to be supplied by thermal conduction through the ice, one can calculate from equation (1) with $\alpha = 1$, that for a surface temperature of, e.g., −30°, the temperature gradient below the surface would be about 50°c/mm. From this example it is evident that in practice the evaporation rates are very much smaller than Φ_{max} and that equation (1) is of no importance in freeze drying.

IV. *Flow resistance between dry material and condenser surface*

The various phenomena determining this resistance are closely related to the way in which the evaporation and condenser spaces are connected. In general, a certain amount of piping

is used for this, so that some pressure drop due to friction may be expected. Additional pressure drops may be caused by restrictions such as the neck of the bottle which contains the material to be dried. In particular, if bacterial filters have to be used to separate the evaporation space from the condenser space, pressure drops may be encountered which become of the order of magnitude of the pressure drop over the dry layer.[6]

Finally, a drop in partial pressure of the water vapour will occur near the condenser surface. This results from the fact that small amounts of air, originating from the frozen material and also from leaks in the apparatus, is entrained by the vapour flow towards the condenser surface. There is thus always an appreciable amount of air near this surface, through which the condensing vapour has to diffuse. Therefore, the location of the discharge line to the vacuum pump with respect to the condenser is of great importance.

Provided something is known about the amount of leakage, for most geometric arrangements frictional and diffusional pressure drops can be predicted on the basis of well-known theories; in this respect, the work of Ede[7] is referred to.

V. *Heat conduction through the ice layer on the condenser*

This layer offers a resistance to heat flow which is proportional to its thickness and inversely proportional to its thermal conductivity. The temperature drop is of the same order of magnitude as the temperature drop in the frozen layer; on drying, the latter decreases and the former increases. In most designs the ultimate average thickness of the ice on the condenser is smaller than the initial thickness of the frozen material, because the condenser surface is generally greater than the evaporator surface. Only with a good vacuum is the ice on the condenser clear with a good thermal conductivity; when the equipment leaks too much or the pumping action is poor, the ice has a frosty appearance and the thermal conductivity may be appreciably lower than for solid ice.[8]

VI. *Heat transfer from the condenser wall surface to the cooling medium*

In the case presented in Fig. 1 the heat has to be conducted through the condenser wall (mostly of metal) and transferred to the cold fluid (forced convection or boiling). At the heat fluxes encountered in freeze drying, the temperature drop in this section is very small.

Alternative ways of removing the water vapour are pumping and absorption of the vapour by a suitable liquid. Both methods have the advantage that the removal may be carried out continuously, whereas with a surface condenser the ice has to be removed intermittently by thawing. If, however, the drying is operated batchwise, which is usually the case, a surface condenser is preferable. With continuous drying, which has hardly left the development stage, the surface condenser, which is continuously cleaned by means of mechanical scrapers, may in the future be replaced by an absorption system. A few aspects of this method will be mentioned in the last section of this paper.

In comparing the various resistances enumerated above, one may say that the drying rate is mainly determined by the phenomena in the sections II–IV. As to section I, it is easy to supply sufficient amount of heat at the maximum permissible temperature of the frozen material. The condenser resistances V and VI can be made relatively small. The condenser temperature is more or less fixed for economical reasons. A lowering of this temperature involves a rapid increase in operating cost, whereas (because of the vapour pressure–temperature relationship) the vapour pressure at the condenser surface decreases only slightly. Economic condenser temperatures seem to be in the range from −30 to −45°.

In many instances it is possible, by adequate design of the space connecting the evaporator and the condenser and by minimizing the leakage, to concentrate nearly all the available temperature drop over the layer to be dried (sections II and III). If during the drying this temperature drop ($t_h - t_c$) is kept constant, the drying rate changes from the initial value φ_1 (determined by the thermal resistance of the frozen layer) to the final value φ_2 (determined by the flow resistance of the completely dried layer). It can be shown that in such a case the drying time, τ_d, is represented by:

$$\tau_d = \frac{d^2 \rho_6^r}{k_f(t_h - t_c)} \cdot f(\Phi_1/\Phi_2)^* \quad \ldots\ldots (2)$$

The value of $f(\Phi_1/\Phi_2)$ not only depends on Φ_1/Φ_2, but also to some extent on the temperatures of the heating and condensing surfaces chosen. For t_h between −5 and −10° and t_c = −35°

*See notation at the end of this paper.

the following approximate values can be calculated:

Φ_1/Φ_2 ..	0	1	3	10
$f(\Phi_1/\Phi_2)$..	0·50	1·3	2·4	6·1

The case, $\Phi_1/\Phi_2 = 0$, corresponds to the evaporation of pure ice where no resistance of the dry material exists. In practice, the value of Φ_1/Φ_2 is greater than one. Incidentally, this has the advantage that the receding ice surface remains flat, whereas for $\Phi_1/\Phi_2 < 1$ small variations in ice thickness would be enlarged during evaporation.

Since the flow resistance of the dried material plays such an important role in the rate of drying, the various factors which influence this resistance have been investigated more closely.

Permeability of the dried material

A number of years ago the resistance of various freeze-dried materials to water-vapour flow was investigated in Delft, in close co-operation with the T.N.O. organization in the Hague. Two kinds of experiments were performed:

(*a*) Sixteen commercial and synthetic liquid substances were spin-frozen in bottles at − 35° and dried in the plasma drying plant of the Central Laboratory of the Blood Transfusion Department of the Netherlands Red Cross Organization in Amsterdam. The 16 materials were contained in 96 bottles and were dried under identical conditions. Drying times were observed and microphotographs were taken of a number of dry samples.

(*b*) For a few substances, the permeability of the dry layer to vapour flow was quantitatively determined in a small experimental freeze dryer, previously used for the determination of the evaporation coefficient, α, of pure ice.[5] In particular, the influence of the rate of freezing on the resistance to vapour flow was investigated.

From these experiments it was found that the structure of the dried material is largely determined by the composition of the starting material and by the rate at which it has been frozen. The permeability to vapour flow depends on this structure, and also on the eventual structural changes occurring during the drying.

Influence of composition

A first indication was obtained from the comparative drying experiments (*a*), where the rate of freezing and the conditions of drying were the same for all substances investigated. These contained various amounts of soluble material (mostly glucose or lactose, and to a minor extent inorganic salts) and of insoluble material (both albumen and fat). Table I gives a survey of the more relevant results obtained.

Table I

Drying times in a plasma freeze-drying plant; glass bottles

($\sim$ 2 cm., $t_c = -38$°C)

No.	Substance	Soluble matter, % wt.	Insoluble matter, % wt.	Average drying time, min.
1	Egg yolk	0·2	39	290
2	Cheese suspension	1·5	39	430
3	Cream	2·9	42	470
4	Churn milk	3·9	4	510
5	Condensed milk	14	20	570

Photomicrographs of the dry samples of numbers 1 to 4 in Table I showed that these consisted of more or less parallel plates which contained the soluble material in the form of small crystals and the solids originally present. The plates were parallel to the heat flux previously applied on freezing, and thus also parallel to the heat and vapour flow on drying. The free space between the plates contained pure ice previous to drying. As a consequence of this particular structure, these dried samples could easily be broken along a plane parallel to the plates. Fig. 2 shows a picture of such a break-plane.

The condensed milk (No. 5) and similar materials (concentrated baby food, ice-mix) showed a more uniform structure. Consequently, these materials have a much higher resistance to vapour flow resulting in long drying times and the development of cracks or rupture of parts of the dried material. The latter effects may involve incomplete drying.

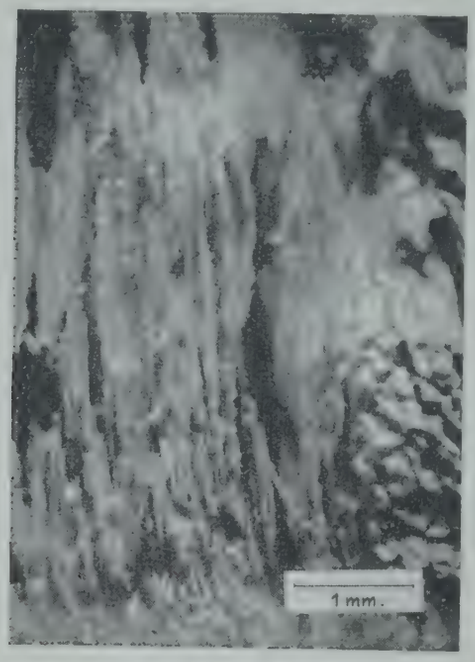

FIG. 2. *Break-plane of freeze-dried churn-milk.*

Combining this information with the data of Table I, shows that the samples containing little soluble material produce a structure resulting in a shorter drying time, whereas the sample with 14% lactose does not. Apparently, the content of insoluble material has little effect. In fact, the concentration of dissolved sugars in Nos. 1–4 is below the eutectic concentration (approx. 10% for lactose), whereas for No. 5 it is higher than this concentration. Thus on freezing the former substances, pure ice and a eutectic mixture containing the insoluble matter are formed. Under certain freezing conditions the flake-like ice crystals cover practically the whole thickness of the frozen layer, so that on evaporation large spaces are available to the transportation of vapour. The vapour coming from the ice in the eutectic structure has to travel through smaller spaces towards the larger ones.

For these conditions (Nos. 1–4 in Table I) the mass fraction of crystallized pure ice, φ, may be calculated from

$$\varphi = 1 - \frac{c_s + c_i}{c_e (1 - c_i) + c_i} \quad , \qquad \text{(3)}$$

where c_s = mass fraction of soluble material in substance to be dried,
c_i = mass fraction of insoluble material,
c_e = mass fraction of soluble material in pure solution at eutectic composition.

It is seen that for $c_i = 0$, φ changes from 1 to 0, as c_s is varied from 0 to c_e. Since the free space available for vapour flow is proportional to φ, it is to be expected that the permeability of the dry layer will decrease as c_s is increased.

In the case of pure suspensions ($c_s = 0$) equation (3) loses its significance since c_e cannot be defined and the insoluble material is concentrated in clusters on freezing. There may, however, be no sufficient cohesion between the suspended particles; in such a case they are blown off the surface during the drying operation.

Permeability to vapour flow of the anisotropic structure

With the dried samples showing a plate-like structure it was found that the distance, D, between the layers containing the solid material was between 30 and 100 μ. Since the working pressure was of the order of 1 mm. Hg with a mean free path of the molecules of about 100 μ, the vapour flow between the plates can be regarded to be mainly Knudsen-flow. In that case the permeability, K, can be defined thus:

$$\Phi = - KM \, dp/dx \qquad \text{(4)}$$

With consistent metric units, K is expressed in

$$\left[\frac{\text{kmole/m.}^2\,\text{sec.}}{\text{N/m.}^3}\right].$$

For molecular flow through a material containing parallel slits of width D, K is found to be:

$$K = \frac{2}{3}\frac{D\bar{u}}{RT}\cdot F \qquad \ldots\ldots (5)$$

The fractional free area, F, of a cross-section perpendicular to flow, is roughly proportional to the mass fraction of crystallized pure ice, φ, so that for otherwise constant conditions:

$$K \propto D\varphi \qquad \ldots\ldots (6)$$

It can be seen from equation (6) that for a constant value of D the permeability increases as φ becomes greater, i.e., as the content of soluble material is decreased [see equation (3)]. This is in qualitative agreement with the observed fact that shorter drying times are obtained for substances with a smaller content of dissolved sugars (Table I). It can also be seen from Table II that the permeability of dried milk (4·8% lactose) is about 3 times greater than the permeability of milk of which the lactose content has been increased to 9·2%. Both substances had been frozen under nearly identical conditions; their φ-values were about 0·4 and 0·1 respectively.

The above theory must be considered as only qualitative. For φ-values near 1 the permeability will be good, but the dry material will also be very fragile. For very small values of φ (say $<0{\cdot}1$) the resistance of the free space may already become of the order of magnitude of the flow resistance of the dried eutectic mixture. Finally, not only has the composition to be considered, but also the average distance, D, between the solid layers. It appears that this distance depends on the freezing conditions.

Influence of the freezing rate

Most of the experiments of type (*b*) have been studies of the influence of the rate of freezing on the permeability. To this end, samples about 4-mm. thick were frozen on a tray which could be cooled at different temperatures. The tray was introduced into the experimental dryer and permeability values deduced from direct measurements of the rate of evaporation and of temperatures and pressures.

The main results have been collected in Table II; here the rate of freezing has been expressed as the average increase of the thickness of the frozen layer per unit time (mm./min.). A freezing rate of 1 mm./min. would involve a temperature gradient of about 2°c/mm. in the frozen substance.

Table II

Permeability to water vapour at different freezing rates

No.	Substance	Freezing rate, mm./min.	Permeability K, 10^{-8} m. kmole/N sec.
1	Standard milk (4·8% lactose)	0·41	0·16
2	„ „	0·53	0·55
3	„ „	0·69	0·33
4	„ „	0·77	0·26
5	Standard milk (diluted 50/50)	0·26	0·27
6	„ „ (+ 4·4% lactose extra)	0·82	0·087
7	Water, containing 5% lactose	0·17	0·69
8	„	0·68	0·38
9	„	0·83	0·22
10	Diluted orange juice	0·50	0·55

In Fig. 3 the K-values of Table II have been plotted against the rate of freezing; Nos. 5 and 6 have not been included because these substances had a different concentration of soluble material. It is seen from Fig. 3 that the permeabilities for milk and lactose solution agree well for freezing rates greater than 0·5 mm./min. That the permeability decreases with a greater rate of freezing* is a consequence of the fact that the average distance, D, between the plates containing the

*This effect has also been observed by Neumann.[9]

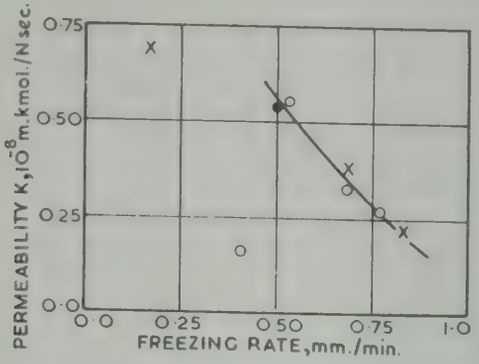

FIG. 3. *Influence of the rate of freezing on the permeability of dry product*
○ milk. × water+5% lactose. ● orange juice.

eutectic mixture becomes smaller [cf. equation (6)]. The explanation for this is that the number of nuclei per unit surface from which ice crystals start growing will become greater as the rate of heat withdrawal is increased.

The permeability for milk at the lowest rate of freezing (No. 1) deviates considerably from the other measurements. During the freezing period it was observed here (and also with No. 5) that the liquid was subcooled to $-8°$ prior to freezing, whereas with the other samples solidification started at subcooling temperatures of the order of $-3°$. Thus, it is believed that in these cases the high degree of subcooling caused a rapid crystallization resulting in a fine-grained and perhaps more isotropic structure.

In summarizing these experiments, it can be concluded that a plate-like structure of dry material, which promotes the permeability to vapour flow, can be obtained with substances in which the concentration of dissolved material is below the eutectic concentration, and at rates of freezing between 0·5 and 1 mm./min. The permeability decreases with increasing concentration of the solution and with increasing freezing rate in the same region. The drying of material containing more dissolved substance than in the eutectic composition is impractical because of the very small permeability; as a result, relatively great pressure drops develop on drying which may cause mechanical changes in the dry material.

The K-values reported here lie between 0·2 and $0{\cdot}7 \times 10^{-8}$ units. The average value reported by Strickland-Constable[6] for blood plasma (~3% dissolved NaCl + glucose + sodium citrate) is $0{\cdot}8 \times 10^{-8}$ units. As to the significance of these values of K, it should be noted that to obtain the same final rate of evaporation (Φ_2) as the initial one (Φ_1) for $t_h = -10°C$ and $t_c = -35°C$, K should have a value of about 8×10^{-8} mks. units. Thus, for the examples treated in this paper the values of Φ_1/Φ_2 are 10 or higher, i.e., the equivalent resistance of the dry layer is many times greater than that of the frozen layer.

Continuous freeze drying

From equation (2) it can be seen that in the batch drying of a particular product under certain circumstances, the drying time, t_d, is proportional to the square of the layer thickness, d. This means that with a given evaporator area the production rate is inversely proportional to d. Since the frequency of loading is inversely proportional to d^2, it is clear that for batch dryers the optimum operation is associated with drying times of the order of hours; this is obtained with layers a few cm. thick and an evaporation flux of the order of 1 kg./m.² h. This figure compares unfavourably with the capacity of liquid evaporators which is of the order of 100 kg. m.² h. The possible economic advantage of a high specific drying rate by using thin layers can only be obtained if the charging and discharging periods can be omitted, i.e., by continuous operation.

Without any attempt at complete analysis of the problems of continuous freeze drying, a few of the major difficulties involved are mentioned below.

(*a*) Since in a continuous operation the conditions at each fixed point in the plant are stationary, the material has to be moved from where it is frozen to where it is removed in dry form. In principle, a similar problem has been solved for vacuum belt- or drum-dryers, although in freeze drying more rigorous requirements have to be set for the vacuum-tightness of the system. Cooling and heating facilities would not present great technical difficulties.

(*b*) A particular problem seems to be that of introducing the liquid feed into the vacuum chamber and transforming it into a thin frozen layer. In orientating experiments, it was possible to produce such a layer by simply spraying the liquid feed in vacuum on a metal surface. While travelling between the spray nozzle and the surface, the drops are subcooled by evaporation, but they solidify only after the metal surface has been hit; for this operation to be successful, the pressure should be below 1·5 mm. Hg, but it is doubtful whether a uniform and controlled layer thickness can be produced. Moreover, the dry structure of the material produced in this way will probably be very fine-grained which involves a low permeability to water vapour.

(*c*) The dry material removed from the moving surface has also to be removed from the drying chamber. This is only possible by intermittent operation.

(*d*) The water vapour produced has to be removed continuously, so that a surface condenser is less suitable. The author has tried continuous condensation of low-pressure water vapour on the surface of a cold organic liquid in view of the prospect of a subsequent easy phase separation of the ice. These experiments were fairly successful as far as heat transfer is concerned, but it appeared that the ice particles formed in the liquid were so small that the separation afterwards was not a very attractive procedure. Therefore, later experiments have been directed towards the absorption of water vapour by de-aerated cold brine solutions. The same principle has been indicated by Martin,[10] who has described a spray absorption tower for this purpose. The conclusion drawn was that a falling film absorber is preferable. For purposes of orientation, an apparatus was designed in which 3000 kg./h. of a 30% $CaCl_2$ solution at -30°C passed down the walls of an annular space between two cylinders; with the circumference of this annulus about 180 cm. and the height 70 cm. it is easily possible to remove 10 kg./h. of water vapour at a pressure of 1·5 mm. Hg with a partial air pressure of 0·15 mm. Hg. Because of the absorption of water, the brine is diluted and special means must be provided to maintain its concentration at a fixed level.

(*e*) A very serious disadvantage of a continuous freeze dryer is the impossibility of keeping the equipment and the product sterile. Thus it seems that for the drying of blood plasma and penicillin, batch drying in bottles or containers, which can be separated from the rest of the plant by means of bacterial filters, will still be preferable. For other products, which do not require sterile handling, it is a question of whether the advantages obtainable with freeze-dried products will outweigh the many technical difficulties of the continuous operation.

Acknowledgment

Much of this work was carried out by the Technisch Physische Dienst T.N.O. en T.H., Delft, in co-operation with Central Technical Department of the organization T.N.O., The Hague. Thanks are due to Ir. A. C. Timmers who carried out the investigations mentioned in section 3, and to Ir. A. H. de Haas van Dorsser, of T.N.O., for his valuable advice.

Notation

c	= mass fraction	—
d	= thickness of layer to be dried	m.
D	= average distance between solid plates	m.
F	= fractional free area	—
k_f	= thermal conductivity of frozen substance	w/m. °C
K	= permeability of dry material	m. kmole/N sec.
M	= molecular mass	kg./kmole
p	= pressure	N/m.²
r	= heat of sublimation	w sec./kg.
R	= gas constant = 8315	w sec./kmole °K
t	= temperature	°C
T	= absolute temperature	°K
$\bar{u}$	= mean molecular velocity	m./sec.
x	= co-ordinate in direction of vapour flow	m.
α	= evaporation coefficient	—
φ	= mass fraction of pure ice in frozen substance	—
Φ	= specific evaporation rate	kg./m.² sec.

ρ_i = density of ice — kg./m.^{3}
τ_d = drying time — sec.

Other units are defined in the text.

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Discussion

Mr. E. J. Rolfe: Prof. Kramers in his paper states that the most important factor governing the drying rate during freeze drying is the permeability of the dry layer, and that, in general, the supply of heat to the frozen material is not a great problem.

It has now been shown that the prolonged drying times of the order of 24–48 h. necessary for the freeze drying of raw beef steaks is due to the supply of heat to the evaporative surface being the limiting factor in the plant used. There have been two recent developments which permit greatly increased heat inputs without thawing the material, and in this way have enabled the drying times to be reduced to 4–8 h.

Brynko & Smithies[1] in Canada impaled the meat between a pair of spiked metal trays, the spikes penetrating through the thickness of the meat. The trays are heated, and the spikes conduct an ample supply of heat into the material, and also provide a large area of evaporative surface.

In the A.F.D. process developed at the Ministry of Agriculture, Fisheries and Food Experimental Factory, Aberdeen, the material to be dried is placed on metal trays and sandwiched between heated flat parallel plates. A good supply of heat is provided by good thermal contact between the plates and material. The factors controlling the rate of drying in this latter process are:

(1) close contact between heating plates and surface of material to be dried provides good heat-transfer but inhibits escape of water vapour from the tissue. If this shows signs of occurring, the degree of contact must be relaxed to prevent thawing. This difficulty is being overcome by modifying the tray design to provide easy escape of water vapour;
(2) the structure of the tissue. The fibrous nature and direction of grain influence markedly the rate of drying. Meat sliced with the grain dries more slowly than that sliced across the grain;
(3) the permeability, i.e. pore size, of the dry external layer.

Any of the above three factors can limit the rate of drying depending on the circumstances.

Prof. Kramers: I am grateful for Mr. Rolfe's additional remarks. Perhaps I should have emphasized the fact that the conclusions in my paper are based on experiments with solutions. There we had no difficulty in obtaining a good thermal contact between the heating plate and the material to be dried. I can very well imagine that in the freeze-drying of meat and similar 'solid' substances the restricted possibility of thermal contact may be the most important factor in determining the drying rate.

Mr. T. W. G. Rowe (Edwards High Vacuum Ltd): In the shelf freezing from below, and the freeze-drying of streptomycin, in layers 11 mm. thick, we have noticed that crystals are formed perpendicular to the surface for a depth of about 8 mm.; below this, the frozen or dried material has a random crystalline or amorphous appearance. At the interface melting occurs during drying. Can Prof. Kramers give me any idea of the critical rate for freezing?

Prof. Kramers: It might be possible that with streptomycin the growth of the ice crystals caused a transport and a concentration of soluble matter; this would result in a lower melting point. Perhaps such an effect could be suppressed by freezing more rapidly. Since our measurements were carried out with layers only 4 mm. thick, no 'critical' freezing rate can be derived from them.

Prof. J. Kuprianoff: In addition to the remarks about the important problem of heat supply to the frozen material during its dehydration in vacuum, I would like to mention the observations made in Karlsruhe on freeze drying of milk in a large heated pan. It has been found that at higher heating rate a very thin water-vapour layer appears between the metal pan—in which the milk was frozen—and the frozen milk block, similar to the well-known Leidenfrost's phenomena on liquids; the vapour escapes through the very narrow channel so formed and the milk-ice block is 'swimming' in this vapour layer. In such conditions a quite high temperature drop may result between the pan and the ice block, which in extreme cases can reach something of the order of 20°C.

Prof. Kramers: We did not find the effect mentioned by Prof. Kuprianoff. In a number of experiments with water we were able to derive the thermal conductivity of ice from the rate of evaporation, the evaporation pressure and the plate temperature. Since the results agreed well with the values from literature, it was concluded that there was no additional heat resistance between the plate and the ice.

Mr. Joyce: I appreciate very much the importance of the eutectic diagram that has been drawn and would like to ask the speaker if he could offer any suggestions on how to obtain such information for complex mixtures of foodstuffs such as apple dice, sugar and citrus pulp.

Prof. Kramers: I agree that the case treated in the paper is very simple and merely meant to illustrate a principle. The results might be applied only qualitatively to more complicated substances.

Mr. Joyce: Prof. Kramers has discussed the possibilities of continuous freeze-drying and stated that the introduction of the material into the drying chamber presents some difficulties. There is one particular material, namely, blackcurrants, which, in our limited experience, may well lend themselves to continuous freeze-drying. If pre-frozen and then passed through an abrasive potato peeler to puncture the rather tough skin, they will freeze-dry quite rapidly.

The rupturing of the thick skin gives a relatively large surface from which sublimation can take place and would appear to be the limiting factor for freeze-drying this type of berry.

Prof. Kramers: Thank you for this valuable remark. This process is somewhat similar to that described in an American patent where frozen pellets are freeze-dried. I do not know whether it has been carried out on a commercial scale; probably the heat transfer to the pellets will not be good.

There was also a rather long discussion between various members of the audience including Dr. Gane, but this was outside the scope of Prof. Kramers's paper. At the close of this discussion, *Mr. Joyce* said: I should like to endorse the remarks made that the puff-drying of pulps is not altogether easy and some careful adjustment of pumping speeds operating vacuum and heat input is required. It has been our experience that raspberry juice brought to 60% solids by the addition of sugar is easier to puff-dry than raspberry juice concentrated tenfold with added sugar to the same total solids concentration, and also that lemon pulp is easier to puff than orange pulp.

Reference

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MOISTURE EQUILIBRIUM AND THE DETERMINATION OF WATER CONTENT OF DEHYDRATED FOODS

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Introduction

Dehydration of foodstuffs is usually effected by subjecting the material to conditions such that water is removed by vaporization. This requires that the partial pressure of water vapour at the surface of the material due to its water content must exceed that in the environment for drying to proceed. These two partial pressures can be more or less independently varied. That exerted by the foodstuff always depends on its composition, water content and temperature; it may also be affected by such factors as homogeneity, state of sub-division, and previous history. For convenience, the partial pressure of water vapour of an atmosphere in thermal and moisture equilibrium with a foodstuff will be referred to as the vapour pressure of the material. It is apparent that some knowledge of the vapour pressures of foodstuffs as a function of water content and temperature is basic to the design of dehydration equipment. Such information is also needed in connexion with the handling, packaging and storage of dehydrated products.

Moisture equilibrium is discussed here in relation to the manner in which water is present in dehydrated foods. Various reference methods which have been proposed for the determination of water content are then examined. Finally, the nuclear magnetic resonance and the heat-of-dilution dichromate oxidation methods for measuring moisture are discussed. This rather limited review of a very broad subject is designed primarily to emphasize the work of a number of present and former colleagues at the Western Regional Research Laboratory whom the present author is privileged to represent at this Conference.

Water vapour sorption isotherms of dehydrated foodstuffs

Most of the moisture equilibrium data available for foodstuffs have been obtained by allowing samples to reach a constant weight when exposed to an environment in which the temperature and water vapour pressure are fixed within narrow limits.[1–3] Either saturated salt solutions[4–7] or sulphuric acid solutions[8] are usually used for maintaining constant relative humidity in a closed vessel either at atmospheric pressure or *in vacuo*. Many days or even months may be required to reach equilibrium, but the time required to transfer water through the vapour phase may be reduced by evacuation or continuous circulation of the conditioned atmosphere over the sample. Reduction of particle size is one method of reducing the time required for transfer of water within the material, and wetting the sample followed by freeze-drying may also produce a material which equilibrates more rapidly.

Another method of obtaining moisture equilibrium data consists of determining the water vapour pressure of samples of various moisture contents. This can be done in a suitable vacuum apparatus in which the vapour pressure is measured directly,[9, 10] or by determining the relative humidity (R.H.) of the atmosphere in moisture equilibrium with the sample by use of a suitable hygrometer.[11, 12] A single determination requires, at most, about an hour, provided equilibrium moisture distribution within the sample has previously been attained. The relative speed of this method is clearly advantageous for reducing thermal degradation reactions during measurements at elevated temperatures.

In a third approach which has been used in some of the most careful studies of sorption isotherms, the material is confined to a high-vacuum system and the gain or loss of moisture brought about by admission or removal of water to the system is followed either by use of a quartz-spiral balance[13, 14] or volumetrically[15] in conjunction with pressure measurements.

The water vapour pressure of the material as a function of its moisture content at a specified temperature constitutes a sorption isotherm. Water content is expressed here in g. of water per 100 g. of dry material. Humidity of the gas phase in equilibrium with the sample is expressed as relative vapour pressure, p/p_0, where p and p_0 are respectively the vapour pressures of the material and of pure water at the temperature of measurement. The terms relative humidity and relative vapour pressure as used here are interchangeable. The terms adsorption

and desorption are used to designate the gain or loss of moisture by the material without implication either as to the nature of the interaction of water with the sorbent or to the distribution of the sorbate upon, or within, the material. Sorption is used when it is either unnecessary or undesirable to distinguish between adsorption and desorption.

Isotherms for a few representative dehydrated foodstuffs are shown in Figs. 1–3. Some of the factors affecting such data will now be discussed briefly.

Moisture equilibrium is difficult to attain at high relative vapour pressures. Presumably all the isotherms tend to increase almost indefinitely in equilibrium water content as the R.H. approaches unity, but approach to equilibrium is slow and growth of micro-organisms is rapid under these conditions. There is also little practical need for accurate data at high R.H. This accounts for the scarcity of isotherm data for foodstuffs at R.H. above about 80%.

The data of Gane[16] for freeze-dried egg white in Fig. 1 were obtained by allowing a dry sample to equilibrate at successively higher R.H., yielding the adsorption curve, followed by equilibration at successively lower humidities, yielding the desorption curve. The failure to equilibrate to the same moisture content at a given R.H. in adsorption and desorption is called hysteresis and is widely encountered in materials of high molecular weight. Due to hysteresis, the vapour pressure at any temperature of a sample of specified moisture content may vary appreciably depending on its recent sorption history. The magnitude of hysteresis effects is determined primarily by the composition of the material, but also depends on the temperature and pre-treatment of the sample. It was found to be small for the isotherms of Fig. 2, but it has been carefully investigated for very few foodstuffs. In systems where isotherm data are reproducible in successive adsorptions and desorptions, the moisture content at a given R.H. is invariably higher for desorption than for adsorption when hysteresis occurs.

Although absolute vapour pressure changes rapidly with temperature, the relative vapour pressure is comparatively insensitive to small temperature changes. The isotherms at 10° and 60° for whole egg powder[16] in Fig. 1 illustrate the fact that increase in temperature always produces an increase in the relative vapour pressure at a given water content. This reflects the greater heat of vaporization of water from dehydrated foods as compared with that of pure water, a subject discussed more fully below. Investigation of sorption isotherms over a range of temperature has apparently been carried out for only a few dehydrated foods.

Comparatively little reliable data have appeared on the effect of the pre-treatment and method of drying on sorption isotherms. Whole egg powder prepared by spray-drying and by freeze-drying were found by Makower[17] to show almost identical isotherms. Gane[16] reported very similar isotherms for spray-dried, freeze-dried raw, and freeze-dried cooked samples both in the case of egg white and egg yolk. These results indicate that denaturation of egg proteins has little effect on moisture equilibrium relations. On the other hand, Makower & Dehority[1] found a large difference in the sorption properties of potatoes which had been cooked 30 minutes in live steam, depending on whether the material was subsequently dried rapidly *in vacuo* at 70° or dried slowly *in vacuo* at 37°. Gane[2] concludes from limited data on potatoes, carrots, and cabbage that pre-drying treatment is likely to have greater influence than the method of drying on the sorption isotherms of dehydrated vegetables. At present it would seem best to assume that pre-treatments which subject a foodstuff to widely different temperature histories may yield products differing significantly in water sorption properties in the absence of evidence to the contrary.

For products such as dehydrated vegetables in which the raw material is inherently rather unhomogeneous in composition, sorption isotherms cannot be expected to be precisely reproducible from one lot of material to another. Detectable variations may be expected for significant differences in composition such as may arise from maturity, variety, and processing treatment. Providing interactions among the components have only minor influence on their moisture equilibrium properties, the sorption isotherm for any product is expected to be a weight average of the isotherms of the constituents. Although necessary data on individual components are not yet available for checking the correctness or the practical utility of thus calculating sorption isotherms, some available data are clearly in accord with this principle. Gane[16] found that the sorption isotherm measured for whole egg powder is in excellent agreement with that calculated from the separately measured isotherms for egg white and yolk. His data also showed that the sorption isotherm of egg yolk calculated on a fat-free basis

differed little from that of egg white. Since fat is expected to sorb very little water, he concluded that the albumen and the yolk proteins have similar sorption properties. The water sorption data of Supplee[18, 19] on milk powder of widely different fat contents also reduce to approximately a common isotherm on a fat-free basis. Gane[2] reported good agreement between measured and calculated isotherms for dried soups prepared by mixing the dried products, but not when the fresh ingredients are mixed prior to drying.

A survey of available sorption isotherm data for foodstuffs (e.g., Figs. 1–3) reveal marked differences both in shape and in amount of water present in the range from 0 to about 0·5 R.H. The sigmoid character of the curves is most pronounced and the moisture content at very low humidities is the greatest for those foods whose dry solids are richest in protein, starch, or other high-molecular-weight polymer, and least for foods high in soluble solids.[2, 20] It is clear that an understanding of the sorption isotherms of foodstuffs is most likely to be acquired by thorough studies of moisture equilibria in pure component substances. Some information available from such detailed investigations is summarized below.

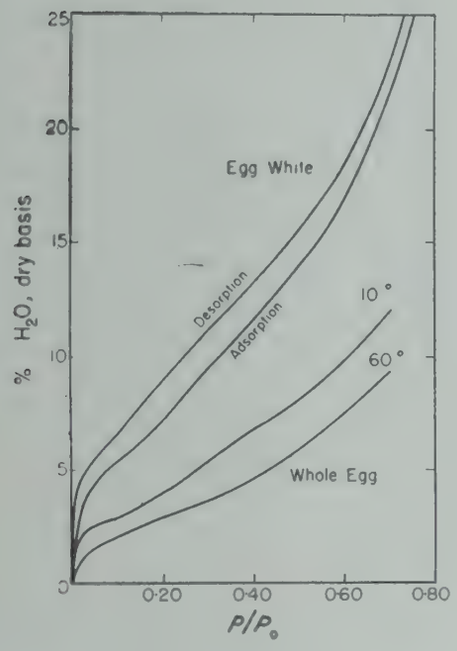


FIG. 1

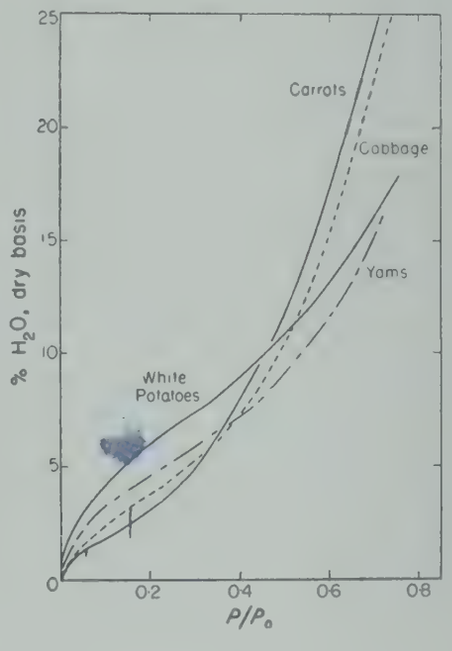


FIG. 2

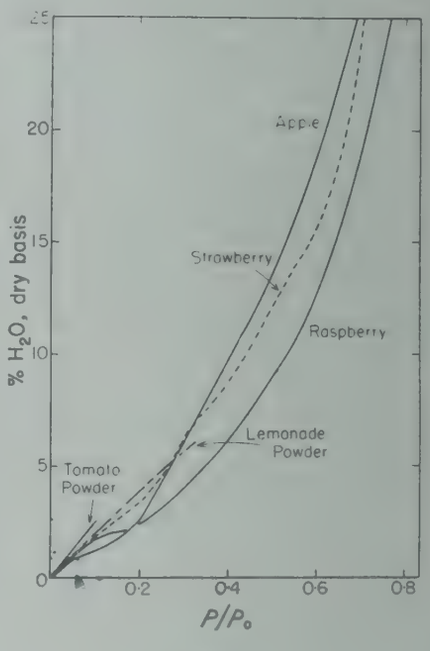


FIG. 3

FIG. 1. *Moisture sorption isotherms for freeze-dried egg white at* 10 C *and of spray-dried whole egg at* 10° *and* 60 C
Data of Gane[16]

FIG. 2. *Moisture sorption isotherms for some dehydrated vegetables at* 37°C
Data of Makower & Dehority[1]

FIG. 3. *Moisture sorption isotherms for some dehydrated fruits and juices*
Sources of data: apple, strawberry, and raspberry, 10 C, Gane[2]; lemonade powder, 21°C, Notter, G. K., Taylor, D. H., and Walker, L. H., *Food Tech., Champaign*, 1955, **9**, 503; tomato powder, 40–65 C, Lazar, M. E., Brown, A. H., Smith, G. S., Wong, F. F., and Lindquist, F. E., *Food Tech., Champaign*, 1956, **10**, 129

Moisture equilibrium in pure components

As already mentioned, fats, being hydrophobic in nature, in general sorb negligible amounts of water. Also in this category are salts and low-molecular-weight crystalline compounds, such as sucrose, which do not form stable hydrates. At very high R.H. these materials, if soluble, would eventually deliquesce, but through most of the humidity range their equilibrium moisture content is about two to three orders of magnitude less than those found for dehydrated foodstuffs. Such soluble constituents may be quite hygroscopic if they are in a non-crystalline condition. Amorphous sucrose was found by Makower & Dye[21] to have the sorption isotherm shown in Fig. 4. The non-crystalline character of this material was confirmed by *X*-ray diffraction measurements.[22] At 25° and a R.H. of 0·12 or less, the amorphous phase remained stable for years but above about 0·3 R.H., crystallization of the sucrose with almost complete loss of moisture content took place usually within a few days.[21, 22]

The tendency of many fruit powders to become sticky or cake is attributed to the presence of sugars in the amorphous form.

Included in Fig. 4 are isotherms for the monohydrates of α-lactose and α-D-glucose and a portion of that for calcium chloride. In these cases the isotherms consist of single values of the relative vapour pressure characteristic of each hydrate. It is interesting that the vapour pressure of the lactose hydrate is less at 25° than that of the hydrate of calcium chloride which determines its drying efficiency. Again it should be emphasized that the sorption isotherm gives no information on how rapidly equilibrium is approached. Thus, crystalline lactose apparently takes up water very slowly even at high R.H.[23] The crystallization of amorphous lactose and formation of the hydrate have been shown[24, 25] to be the explanation of the uptake of moisture by milk powder with subsequent loss of a portion of the water when held at relative humidities above about 0·4.

Sorption isotherms for potato starch gel,[26, 27] egg albumen,[28] pectin[29] and cellulose[30] are shown in Fig. 5 as typical of the various types of high-molecular-weight components occurring in foodstuffs. The isotherm for cellulose is that for native cotton fibres; regenerated cellulose shows an isotherm of the same shape but about twice the water content at the same R.H.[31] Heat-denatured egg albumen showed a sorption isotherm which differed only slightly from that for crystalline or freeze-dried material.[28]

Of the three types of isotherms of Figs. 4 and 5, that of crystalline hydrates with large isobaric changes in moisture content is probably of least practical importance in most dehydrated foodstuffs. The sorption of water vapour by amorphous sucrose can be described simply and probably reasonably accurately over the low R.H. range as a solid solution in which the content of the volatile component follows Henry's Law. In accordance with this view, the isotherm over the entire humidity range may be regarded as a system which deviates from Raoult's Law in a manner characteristic of preferred mutual interaction between the two components.[32]

A few years ago in a review of the sorption of water vapour by proteins and polymers, McLaren & Rowen[33] stated that ' at present no theoretical approach adequately covers the

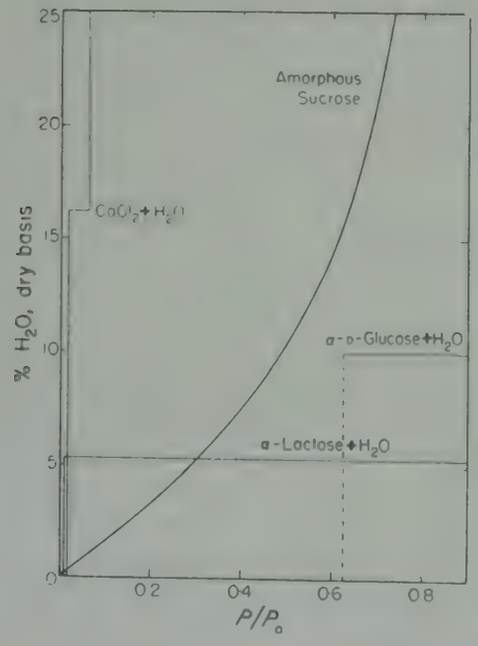


FIG. 4. *Moisture sorption isotherms of some crystalline hydrates and of amorphous sucrose at* 25°C

Sucrose data of Makower & Dye[21] Vapour pressure of lactose hydrate from (log p *vs.* $1/T$) extrapolation of data of Herrington, B. L., *J. Dairy Sci.*, 1934, **17**, 595. Vapour pressure of glucose hydrate is uncertain. Value shown is an upper limit based on observations of Sokolovsky.[23]

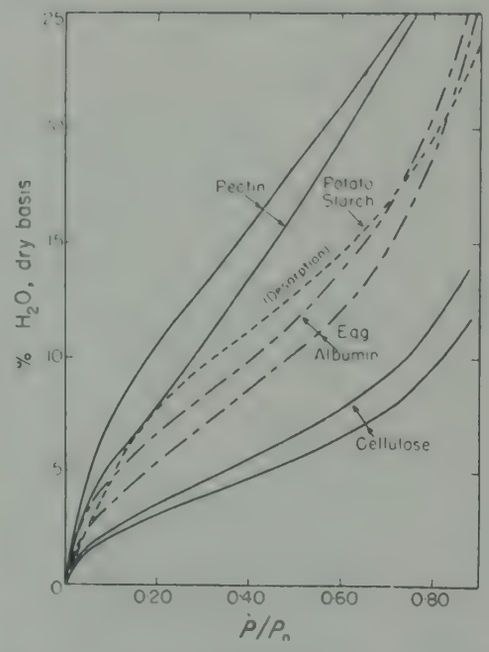


FIG. 5. *Moisture sorption isotherms of some components of foodstuffs*

Sources of data: potato starch gel, 25°C, Fish[26]; egg albumen, 25 °C, Benson & Richardson[28]; pectinic acid, 25 °C, Palmer *et al.*[29]; cellulose (native cotton), 20 °C, Urquhart & Williams.[30]

problem of how water is held by polymers over the entire relative vapour pressure range.' This statement is still applicable. No attempt will be made here to review the extensive literature on this subject, but an effort will be made to indicate how interpretation of sorption equilibrium data has contributed to a partial understanding of systems such as those of Fig. 5. The recent work of Fish[26] on potato starch gel furnishes an excellent example as a basis for this discussion.

Thermodynamics of sorption

Thermodynamic quantities pertaining to the sorption process can be found from the temperature dependence of sorption isotherms. At equilibrium, the Gibbs chemical potential (partial Gibbs free energy) for water must have the same value throughout the system. Specifically this quantity then must be the same in the solid material as in the vapour phase with which the solid is in equilibrium. With reference to liquid water as a standard state, the change in the partial Gibbs function per g. of water for transfer of an infinitesimal quantity from the pure liquid (vapour pressure p_0) to equilibrated solid with vapour pressure p is

$$\Delta\bar{g}_w = \frac{RT}{18} \ln (p/p_0) \quad \ldots\ldots (1)$$

The corresponding change per g. of sorbent referred to dry material as a standard state is found by application of the Gibbs–Duhem relation

$$W\mathrm{d}(\Delta\bar{g}_w) + (1 - W)\,\mathrm{d}(\Delta\bar{g}_s) = 0 \quad \ldots\ldots (2)$$

where W designates the weight fraction of water in the equilibrated sample and subscript s denotes the sorbent. Hence

$$\Delta\bar{g}_s = -\int_0^p \left(\frac{W}{1-W}\right) \mathrm{d}(\Delta\bar{g}_w) \quad \ldots\ldots (3)$$

The over-all change in the Gibbs function for the entire process of dry sorbent combining with water to form 1 g. of equilibrated material with vapour pressure p is

$$\Delta\bar{g} = W\Delta\bar{g}_w + (1 - W)\Delta g_s \quad \ldots\ldots (4)$$

The dependence of the vapour pressure on temperature for an equilibrated sample of fixed moisture content is related to the differential heat of wetting by

$$\left[\frac{\partial \ln (p/p_0)}{\partial T}\right]_W = -\frac{18\Delta\bar{h}_w}{RT^2} \quad \ldots\ldots (5)$$

Here $\Delta\bar{h}_w$ is the change in the partial heat function per g. of water for sorption of an infinitesimal quantity from the pure liquid to equilibrated material of water content W. It is the difference between the heats of vaporization of water from the sorption sample and from pure water. The heat function quantities $\Delta\bar{h}_s$ and Δh may then be calculated in the same way as outlined above for the corresponding Gibbs free energy quantities. The entropy functions are then found from

$$T\Delta s = \Delta\bar{h} - \Delta\bar{g} \quad \ldots\ldots (6)$$

for each component or the corresponding equation for the over-all process. All the above quantities may be put on a molar basis by multiplying by the molecular weight, but it may not be clear what effective molecular weight to use for the sorbent.

These thermodynamic relations assume that the state of the system is defined by the temperature and the composition, whereas hysteresis signifies the absence of thermodynamic equilibrium or the existence of metastable states.[34] Adsorption and desorption data will accordingly lead to somewhat different calculated values of these quantities, but this does not seriously affect their qualitative or rough quantitative interpretation.

The thermodynamic partial quantities for water in potato starch gel determined by Fish[26] from desorption data are presented in Fig. 6. The values of $\Delta\bar{g}_w$ and $\Delta\bar{s}_w$ become respectively negatively and positively infinite as the dry state is approached. If the sorbed water were thermodynamically equivalent to liquid water, the heat of wetting would be zero. Dry potato starch gel is seen from Fig. 6 to have a differential heat of wetting of about 270 cal. g. or

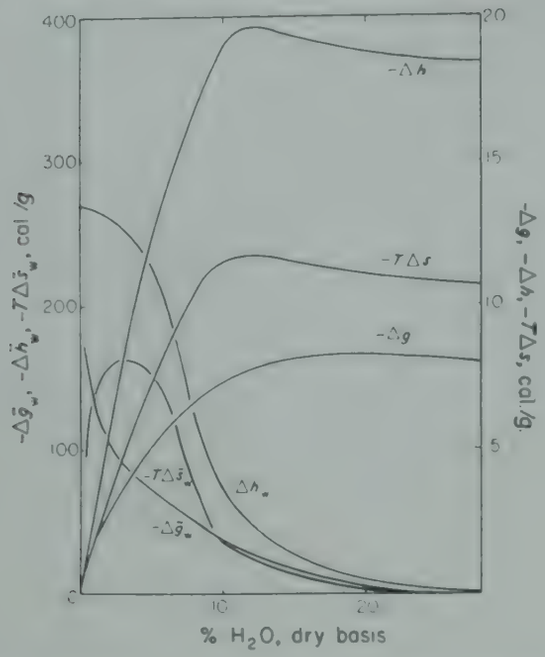


FIG. 6. *Thermodynamic quantities calculated by Fish*[26] *from moisture sorption isotherm data for potato starch gel*

The left-hand scale applies to the partial quantities per g. of water. The right-hand scale applies to the integral quantities for the process of mixing appropriate amounts of starch and water to form 1 g. of mixture with the indicated composition. $T=298°K$.

4·9 kcal./mole. Corresponding values of about 3·0 and 4·5 kcal./mole were found in the same way for egg albumen[35, 36] and soda-boiled cotton.[37–39] When calculated from calorimetric measurements of heats of wetting, a value of 4·2 kcal./mole was found both for dry native cotton and regenerated cellulose in the form of viscose rayon.[40] Values in the range of 3 to 6 kcal./mole have been found for other proteins[35, 36] and confirmed calorimetrically[41] for egg albumen and bovine serum albumen.

Hydrogen bonds are known to have energies in this range. Since there are on the average just over 1·5 hydrogen bonds per molecule in liquid water,[42] the above differential heats of wetting suggest that the first water adsorbed by dry material forms two hydrogen bonds each of which is somewhat stronger than those in water.[38, 39] Values of 3 to 7 kcal. per mole of water have been found for heats of hydration of crystalline sugars to form crystalline hydrates.[43]

The differential heat of wetting for potato starch (Fig. 6) drops rapidly as water is adsorbed in the region where the isotherm straightens out. This also applies to the other materials cited above, values of at most a few hundred calories per mole characterizing sorption in the nearly straight-line portions of the isotherms at intermediate relative humidities. Qualitatively this indicates that the sorbed water is bound by energies characteristic of hydrogen bonding in the low-moisture region, but each material has a limited capacity for binding water with such strength.

The partial molal entropy of water in potato starch gel is also seen to have rather high negative values at low moisture contents and decreases in magnitude with increasing hydration in a manner similar to the differential heat of wetting. This decrease in entropy indicates an increased degree of orientation and rigidity of the water molecules in the sorbed state over that in liquid water. The maximum decrease in entropy of −10·9 entropy units at low moisture levels is about twice the entropy decrease for the freezing of water (−5·3 e.u.). Similar decreases in partial molal entropy and correlation with heats of wetting are found in other cases.[36,37]

The values of Δg, Δh, and $T\Delta s$ for the formation of 1 g. of mixture from various proportions of water and dry starch (Fig. 6) show minima which occur at about 10 g. of water per 100 g. of dry starch for Δh and $T\Delta s$. This composition corresponds to one molecule of water per glucose residue. In the absence of interaction between the starch and water, the entropy change for mixing would be positive rather than negative.

Sorption theories

The discussion to this point has been concerned solely with interpretation of thermodynamic quantities obtainable from sorption isotherm data. Considerable effort has been devoted to the development of quantitative theories to account for sigmoid isotherms. The first theory to meet with considerable success was the multimolecular adsorption theory of Brunauer *et al.*[44,45] now commonly called the BET theory. The model serving as a basis for its development assumed

that van der Waals' forces can account for adsorption of gas molecules on the surface of the solid adsorbent, that more than one layer of sorbate molecules may be present on the surface, that the energy of sorption for molecules in all layers except the first is the heat of condensation of pure sorbate, and that the energy of sorption is the same for all molecules in the first layer. Many sigmoid isotherms are found to be fitted by the BET equation in the range of relative vapour pressure from about 0·05 to 0·5 and from this fit is obtained the value of a parameter, n_1, representing the number of molecules of sorbate required to form a monomolecular layer on the surface of the adsorbent. Multiplication of n_1 by the effective cross-sectional area of the sorbate molecule then yields the surface area of the sorbent. The agreement of areas found in this way when various non-polar gases are used as sorbates has established this method as one of the most reliable for measuring surface areas of solids.[15,45]

Subsequently the BET equation was derived by statistical mechanical methods on the basis of a somewhat more general model in which n_1 now represents a number of localized sorption sites accessible to the gas.[46,47] The value of n_1 is found to correspond usually to the sorbate content at the low relative vapour pressure end of the linear portion of the sorption isotherm,[48] i.e., at a R.H. in the neighbourhood of 0·1 to 0·2 in the curves of Fig. 5. Interpretation of sorption equilibrium data for egg albumen in terms of BET theory has shown that n_1 for water is not only much larger than for nitrogen as sorbate,[49] but is independent of the degree of subdivision for water[50] and other polar gases[51] but not for non-polar gases.[52] This means simply that in this case sorption of polar gases is not a surface phenomenon but involves penetration of the sorbate throughout the solid sorbent. This is true in general for sorption of water by proteins, cellulose, starch, pectin and other natural polymeric materials which show relatively high moisture-sorption capacities usually accompanied by swelling.

Bull[53] interpreted his moisture equilibrium data for a number of proteins in terms of BET theory. From the approximate agreement of the n_1 values thus obtained with the number of amino-acid side-chain polar groups present, Pauling[54] concluded that the dry protein first adsorbs water by the attachment of one molecule of water on each polar amino-acid side-chain. Subsequently considerable work has been done on the correlation of the amounts of water sorbed with appreciable heats of wetting with the number, type and accessibility of polar groups in proteins and other polymeric adsorbents.[33] These studies in general support the picture that the more firmly bound water is attached to polar groups in the sorbent by hydrogen bonds.

Most real systems of interest are obviously more complex than the models on which the BET equation has been derived. Sites with various energies of sorption, allowance for swelling of the sorbent, limitations on the number of layers adsorbed, variations in the sorption energy of successive layers and treatment of the system as a solid solution at high R.H. are some of the numerous extensions and variations of models for which quantitative sorption relations have been obtained.[33] Despite the inadequacies of present quantitative theories of sigmoid isotherms, the qualitative picture of sorption on polar sites involving hydrogen bonds combined with multilayer sorption involving van der Waals' forces appears to be essentially correct for moisture equilibrium in the high-molecular-weight components of foodstuffs.

In addition to the information concerning the interaction of water with solids obtainable solely from the interpretation of sorption isotherm data, much additional or corroborative information has been obtained from studies of other properties of these systems as a function of moisture content. Among these may be mentioned density or partial molal volumes, *X*-ray lattice spacings, elastic constants, electrical conductivity, heat capacity, dielectric properties, moisture diffusion coefficients and nuclear magnetic resonance absorption. Unfortunately these findings are much too extensive to be discussed here.

Determination of water content

The moisture contents found necessary for good stability in dehydrated foodstuffs usually correspond to relative vapour pressures of the order of 0·10 or less. In terms of the above discussion of sorption isotherms, these moisture contents are in the region where the heat of wetting is appreciable and the mobility of the adsorbed water is presumably low. From the thermodynamic point of view, the water vapour pressure furnishes a measure of the chemical potential of moisture in a dehydrated product, and hence would appear to be a logical quantity to measure in relation to storage properties. Makower[55] has recommended its use and

discussed its advantages as a more significant index of stability than moisture content. By reason of the differences in the sorption isotherms of the various components, the moisture is presumably distributed among them so that each has the same water vapour pressure rather than the same water content. Variations in composition may then produce different over-all moisture contents all of which correspond to the same vapour pressure, to the same moisture contents for individual components and hence presumably to the same likelihood of deterioration reaction in the most sensitive component.

The availability of adequate methods for determining moisture content was tacitly assumed in the above discussion of sorption isotherms. Even more basic is the assumption that the water content in foodstuffs or their individual components is a well-defined quantity. In view of the information outlined above concerning the nature of the interactions between water and non-aqueous constituents, a conceptual definition may be made on the basis of the number of units of H_2O present in which the two H-nuclei and the O-nucleus have, within specified limits, the same internuclear distances as in water, but such a definition has real significance only if it can be applied by an appropriate experimental method. Since this condition does not seem to be met at present, it must be concluded that water content is now defined in terms of experimental techniques. When identical results are obtained by techniques which are basically different in their approach, the inference may be drawn that each of these techniques is measuring the same quantity, but it may be difficult to establish that this quantity is the same as that of the conceptual definition.

Some of the pertinent factors affecting the choice of a method for measuring water content are as follows:

1. Accuracy
2. Precision or reproducibility
3. Time to obtain a result
4. Availability of necessary equipment
5. Degree of skill or training required
6. Man-hours per sample
7. Moisture range of interest
8. Suitability for large numbers of analyses
9. Destructive or non-destructive
10. Adaptability for automatic process control
11. Sample size in relation to sampling problem

The relative weights given to these different criteria vary with the purpose for which, and the circumstances under which, the analyses are performed. This discussion is limited to some absolute reference procedures and to two indirect methods initiated at the Western Regional Research Laboratory.

The first four criteria are usually decisive in choice of a reference method. Of these, accuracy is probably the most important and certainly the most difficult to appraise. By accepting one technique as defining, it is clear that the accuracies of other techniques may be judged by comparison, but it appears that no single technique is acceptable in practice as defining water content for all types of foodstuffs. Instead, accuracies of various absolute methods of measurement tend to be judged by either the absence of, or adequate corrections for, sources of error recognizable in terms of some conceptual definition such as the one suggested above. This is the basis on which accuracies of moisture methods are discussed here.

So far as the author is aware, there exists no satisfactory absolute method applicable to foodstuffs in which the water content of the sample is not altered in the course of the determination. The absolute methods now available are based on the principle of complete removal of water from the sample by vaporization, by extraction, by chemical reaction, or by a combination of these processes. Complete removal implies the reduction of the activity of water in the sample to zero. If there are reversible reaction systems present in which water is a product and in which establishment of equilibrium is not extremely slow under the conditions of the desiccation process, this raises the possibility that the removal of water promotes such reactions with the net result that a portion of the water removed was not originally present as H_2O molecules. For convenience, let the water formed in this way be referred to as Le Chatelier moisture in order to distinguish it from degradation moisture, which is defined as water either formed or consumed during the analytical procedure by irreversible chemical reactions. Le Chatelier moisture would be considered a source of error in the determination of water content in the light of the conceptual definition suggested above, but might not be so considered

if a definition based on the amount of moisture available for chemical reactions during storage were adopted. Degradation moisture would be considered a source of error on either basis. The contribution of Le Chatelier moisture to the water content of foodstuffs as determined by any experimental procedure has not been shown to be measurable. Where precise agreement is obtained between procedures which differ markedly in the conditions for removal of moisture from the sample, the absence of Le Chatelier moisture would seem to be a valid inference.

The reference methods discussed here are vacuum-drying, entrainment distillation, and the Fischer volumetric method. Each of these assume[55] that (1) removal of water from the sample is complete, and (2) effects of chemical side-reactions occurring during the removal of water either are negligible or are adequately taken into account. Both the thermodynamic and kinetic aspects of the removal of water are of major importance and require separate discussion.[55–57]

Vacuum drying methods

Equilibrium moisture content

The sigmoid isotherms characteristic of most foodstuffs indicate that there is no clearly defined R.H. greater than zero corresponding to zero equilibrium moisture content. A sample which has attained moisture equilibrium in a vacuum-drying environment has a residual water content determined both by the R.H. maintained and by the slope of the moisture sorption isotherm at this low relative vapour pressure. In the case of potatoes, Makower[55] estimated a residual water content of about 1% if moisture equilibrium were attained at R.H. = 0·005 at 24°. Accordingly, for an equilibrium water content of less than 0·01%, the R.H. at 24° would need to be less than 5×10^{-5}, corresponding to a partial pressure of water vapour of about 1μ. Clearly either a high-vacuum system or a desiccant is required to effect drying to this extent at room temperature.

The rate of increase in vapour pressure with increase in temperature is greater the higher the differential heat of wetting (Equation 5), hence is greatest in the very low moisture range. Using a differential heat of wetting of 5 kcal./mole, about that found for dry potato starch gel,[26] the R.H. and corresponding partial pressures of water vapour at selected elevated temperatures are shown for dehydrated potato with 0·01% equilibrium moisture content in Table I. These are based on the 24° figures shown in the table. (Had the decrease in heat of wetting with increasing temperature been taken into account,[58] the higher temperature values of Table I would be lowered somewhat.) Not only does the R.H. corresponding to this low water content increase with rising temperature, but the rapid rise in vapour pressure of the material relaxes considerably the pressure requirements for vacuum-drying at elevated temperatures. The figures for p and p/p_0 of Table I would be increased tenfold for 0·1% equilibrium water content. Even if this higher residual moisture level be accepted, partial pressures of water vapour of about 1 mm. or less are required below 100°C. Such performance is probably not attained with most commercial vacuum ovens without the use of a desiccant.

Table I

Estimated temperature dependence of the vapour pressure of potato containing 0·01% of water

Temp., °C	Relative humidity, p/p_0	p, mm. Hg
24	(0·00005)	(0·0011)
50	0·00010	0·0091
75	0·00017	0·050
100	0·00028	0·21
125	0·00043	0·75

Rate of approach to equilibrium

The above considerations of vapour pressures of the sample corresponding to various upper limits of residual moisture content which may be acceptable in a reference method give no information on how long may be required to approach moisture equilibrium between the sample and its vacuum environment. Extremely low diffusion coefficients are characteristic of the movement of moisture in most dehydrated foods. The low rates of hot-air drying of cut vegetables in the low-moisture range have been shown to be limited by diffusion of moisture within the material.[59] The low diffusion coefficients found by Fish[26] in potato starch gel have

already been cited. Vacuum-drying to constant weight can require months at room temperature[1,60] and days at temperatures[60,61] of 70° or 75°C even for samples of small particle size.

Methods used to accelerate removal of water at low moisture levels where the rate is diffusion-limited have either reduced the diffusion path-length or have increased the diffusion coefficient. The effect of particle size on drying rate is well illustrated by the 70° vacuum oven data of Makower & Myers[9] on dehydrated carrots (Table II).

Table II

*Variation of apparent moisture content of dehydrated carrots with particle size and time of drying in vacuum oven at 70°C**

Particle-size distribution†	Loss of weight: As apparent % H_2O at various drying times			Loss of weight: As % H_2O after regrinding to 40-mesh,** 44 h.
	6 h.	22 h.	44 h.	
Passes 5-mesh and retained on 10-mesh	2·7	4·3	5·2	6·5
Passes 10-mesh and retained on 18-mesh	3·2	4·6	5·6	6·3
Passes 18-mesh and retained on 35-mesh	3·9	5·2	5·9	6·2
Passes 35-mesh	5·2	5·9	6·1	6·2
Maximum differences among different fractions	2·5	1·6	0·9	0·3

*Data by Makower & Myers.[9]

†Distributions prepared from single lot of diced dehydrated carrots by grinding through food chopper and separating ground material into fractions by sieves.

**Each fraction ground again to pass 40-mesh sieve before drying.

The data in the last column of the table eliminate variations in moisture contents of the different sized particles as a major factor contributing to the observed differences in drying rates, but there is a practical limit to the feasibility of increasing drying rates by grinding and adequate precautions are required to prevent change in moisture content. This subject has been treated in some detail by Makower *et al.*[60] who concluded from experience with dehydrated carrots and potatoes that little is gained by grinding finer than is required to pass a 40-mesh sieve.

The exponential dependence on temperature of the diffusion coefficient at low moisture levels found by Fish[26] for potato starch gel indicates that increased diffusivity of moisture is a major reason (together with increased vapour pressure) for the faster drying rates observed at elevated temperatures.[60] A procedure which increases the permeability of the sample to moisture without requiring elevated temperatures would have the decided advantage of minimizing side reactions, as does the lyophilization procedure of Makower & Nielsen.[62] Essentially it consists of wetting the sample with a relatively large amount of water followed by freeze-drying to a low moisture content. The swollen structure of the moist sample is preserved in the frozen state and the high moisture permeability of the porous freeze-dried product enables complete removal of water to be effected more rapidly or under milder conditions. For example, samples of dehydrated potatoes subjected to the lyophilization procedure reached constant weight over magnesium perchlorate in vacuum desiccators in about 4 days[62] compared with more than 6 months[60] required for similar samples prepared by grinding to pass a 40-mesh screen. Although there would seem to be no reason to expect that the lyophilization procedure would produce any major change in the characteristics of the sorption isotherm at very low moisture contents, this point has not been investigated.

Primary reference method

The definition of water content of a sample, which appears to be most widely accepted as one which is capable of experimental application, is the quantity of water which can be removed at room temperature. In practice this is often taken to be the loss in weight when exposed *in vacuo* to an efficient desiccant at room temperature.[60] Since this makes the assumption that no loss in weight has occurred due to the presence of a volatile component other than water, this method does not furnish an acceptable definition when a non-aqueous component of significant volatility is known to be present. When application of the room-temperature desiccation method requires a long period of time, the assumption that no side reactions are involved may be questioned. The dependence of many such degradation reactions on water

content indicates this is not likely to be a source of significant error since the moisture level is usually very low over much of this time period. The lyophilization procedure[62] can frequently be used to shorten greatly this period and may make it feasible in some cases to use high-vacuum apparatus and gas volumetric procedures for measuring the water content.[15, 63, 64]

Use of elevated temperatures in vacuum drying immediately raises questions as to the extent to which degradation reactions take place and to the removal of volatiles other than water. The problem of removal of non-aqueous volatiles can be investigated by collecting all volatilized material in low-temperature traps and either determining the non-aqueous content or, if more convenient, the quantity of water in the condensate, but application of either entrainment distillation or the Fischer method is more likely to be considered when non-aqueous volatiles are encountered. Elimination of errors due to thermal degradation reactions has been attempted either by choice of a drying temperature low enough to overcome their effects or by adopting a procedure in which allowance is made for them.

Lyophilization procedure

A loss in weight which reaches a maximum value and shows no further increase with continued heating *in vacuo* has frequently been interpreted as indicating no interference from degradation reactions. It has long been known[65] that the maximum weight loss observed varies with the drying temperature in the case of many materials of biological origin. Such variations may arise in some cases from change in equilibrium moisture content with the temperature in the particular apparatus employed; in others they may represent different stages of decomposition. If, however, the maximum loss of weight found for a particular material at an elevated temperature agrees with that found at lower temperatures where the effect of degradation is known (or assumed) to be negligible, the higher-temperature procedure can then be accepted as a satisfactory secondary reference method for that material. In this way Makower & Nielsen[62] showed that vacuum-drying at either 60° or 70° of lyophilized samples of dehydrated beets, white potatoes, and sweet potatoes produced maximum weight losses in about 24 hours agreeing (within 0·1% moisture) with those found by their primary reference method, the room-temperature vacuum-desiccator technique. When these same dehydrated vegetables were dried *in vacuo* at 60° and 70° without lyophilization, in the form of granules that would pass a 40-mesh screen, drying times of the order of 100 hours were required to reach a constant weight[60] and the weight loss exceeded that found for the lyophilized samples.[62] These observations were interpreted[55] as showing that significant degradation occurred in the unlyophilized samples during the drying period because of the much longer time required to lower the moisture content to a level where degradation is negligible at these temperatures.

Redrying procedure

Even when lyophilized, some products cannot be vacuum-dried at sufficiently low temperatures to eliminate adequately the effects of degradation reaction without requiring too much time to allow the procedure to be a useful secondary reference method. Makower *et al.*[60] developed a 'redrying procedure' which may serve this purpose for such products. The object of the procedure is to determine what drying time at a specified temperature is required to produce a loss in weight of the sample equal to its original water content despite simultaneous loss in weight arising from degradation reactions. The procedure consist of three steps: (1) The prepared sample is dried *in vacuo* at a temperature where degradation is not rapid. A drying curve is determined from the loss of weight after various time intervals. The drying time is continued until the sample is assumed to be completely dry. (2) The dry sample is allowed to sorb a known weight of water in a humidistat, preferably a quantity close to the loss in weight of the original sample. Time is allowed for this water to approach an equilibrium distribution in the material. (3) A drying curve is determined for this rehumidified sample under the same conditions as the original drying curve. Provided the first and second drying curves are the same except for a shift in origin, the time required in the second drying to obtain a weight loss equal to that gained in humidification of the dry material is taken as the correct drying time. The weight loss at the corresponding time during the first drying is taken as the water content of the original material. If the condition of identical drying curves (except for a shift in origin) for the first and second drying is not satisfied, too much decomposition is assumed to have occurred and a lower drying temperature is indicated.

The application[60] of this method to the vacuum drying of carrots at 70° is illustrated in Fig. 7. The two drying curves are found to differ by a constant loss of weight at all times, no shift in the time scale being required to make them superimposable. (This was true in all cases investigated.) The amount of water added prior to the second drying was 5·3% in this case. The time for a loss in weight corresponding to this amount to occur in the second drying was 30 hours. The water content of the original sample is then 4·3%, the loss of weight after 30 hours in the first drying. The original drying and redrying curves for cabbage at 70° were found to differ in shape, but at 60 they were identical except for a shift in the loss-of-weight scale. A drying time of 30 hours at 60° was found in this case.

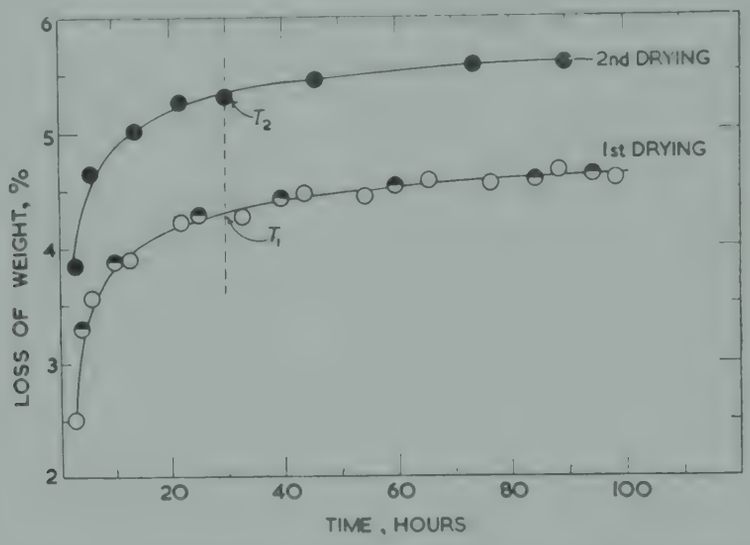


FIG. 7. *Drying and redrying curves for carrots at* 70°C in vacuo
Data of Makower, Chastain, & Nielson.[60]
○ First drying. ● second drying. ⊖ second drying, translated.

The first assumption in the redrying procedure is that all moisture has been removed in the first drying. The long first drying period (about 100 h.) and the low rate of loss of weight (0·005% per h. or less) at the end of this period make this assumption plausible. Extending the initial drying period an additional 40 to 50 hours was found not to change the redrying time. The second assumption, that the two drying curves are essentially the same, is verified in the procedure. The further assumption is implicit that negligible decomposition occurs in drying the sample from the higher to the lower of the initial moisture contents at the start of the two drying curves.

The suitability of the redrying procedure as a secondary reference method was verified[55,60] by comparison of water contents based on drying times determined by this procedure with those found by the primary reference method. Differences in water contents by the two procedures did not exceed 0·2% for three samples each of potatoes and carrots or 0·1% for one sample each of cabbage and onions. A further comparison was later made[55] after the lyophilization procedure was developed with the results shown in Table III. It is observed that all three procedures agree usually to within 0·1% moisture.

Table III

Comparison of moisture determinations by primary and secondary reference methods

	Lyophilized samples*			Unlyophilized samples	
	Vacuum desiccator, room temp.	Vacuum oven		Vacuum oven, 70°C	
		60°C	70°C		
	% H_2O	% H_2O	% H_2O	% H_2O	Time,† h.
White potatoes	8·7	8·8	8·8	8·8	60
Sweet potatoes	8·2	8·2	8·2	8·3	120
Carrots	7·2	7·5	‡	7·3	33
Beets	6·7	6·9	6·8	6·8	100

*Moisture determined by drying to constant weight.
†Drying times determined by redrying procedure.
‡Does not reach constant weight

Reversibility procedure

Sair & Fetzer,[66] in their extensive investigations on the determination of moisture in corn (maize) and products of the wet milling industry, employed what they termed a reversibility procedure for correcting for thermal degradation reactions. It consists of comparing the equilibrium moisture content (regain) under specified conditions of temperature and R.H. of a sample which has been dried at an elevated temperature with that of a control sample which has been dried at a lower temperature at which it is known that no degradation occurs. The difference in these two regains is taken as the loss in weight due to thermal degradation experienced by the sample dried at the higher temperature. For example, samples of ground corn (40-mesh) were dried for various times in a vacuum oven at 100°, after which they were remoistened and dried along with control samples in a vacuum oven at 40° for 340 hours. The sample which had been at 100° for 22 hours showed losses in original weight of 11·90 and 10·82% for the high- and low-temperature dryings, whereas the control showed 10·41% loss in weight. 0·41% is taken as the loss in weight due to decomposition at the higher temperature, giving 11·49% as the water content. Excellent agreement was obtained with values so calculated for drying times ranging from 16 to 72 hours at 100°, the corresponding range of corrections for decomposition losses being 0·33 to 0·50%.

It is assumed in this method that drying at the elevated temperature has not changed the moisture sorption properties of the material at the lower temperature. It is further assumed that none of the loss in weight at the higher temperature is due to non-aqueous volatile matter. In the case of corn, these assumptions appear to be correct since good agreement was found among results determined by the reversibility procedure, by benzene or toluene distillation, and by vacuum-drying over P_2O_5 at 38° and at 50°.

Entrainment distillation methods

Vacuum-drying methods are not usually satisfactory for determining moisture in samples containing volatile components other than water. In the entrainment distillation method, the water removed from the material is collected and measured directly. The development of apparatus and techniques and the applications of distillation moisture methods were reviewed a few years ago by Fetzer.[67] The theory of the procedure has been examined by Overbeek & Mossel[57] as part of an evaluation of entrainment distillation as a reference method for the determination of the water content of foods.[57,61,68]

The discussion concerning the equilibrium and kinetic aspects of the removal of water presented earlier in relation to vacuum drying methods applies also to distillation entrainment. The activity of water in the liquid surrounding the sample in the still plays the same role as environmental relative humidity in vacuum drying. Analysis[57] of steady-state conditions in the distillation method indicates that the water vapour partial pressure (p_{H2O}) ultimately attained in the still is determined entirely by the solubility of water in the entrainment liquid at the mean receiver temperature. On this basis, paraffin hydrocarbons have been recommended as entrainers rather than aromatic or chlorinated hydrocarbons.[57,69] The solubility of water in *iso*-octane (b.p. 99·4°), the entrainer chosen for their work, was estimated to be the same as in *n*-heptane (b.p. 98·7°), viz., 0·055% at 60°, the approximate mean temperature of their receiver at the end of the distillation period. This composition corresponds to p_{H2O} = 2·4 mm. Hg. In an earlier study,[70] Mossel found the residual moisture content of biocolloids and foods dried at 102° in a ventilated air-oven with p_{H2O} = approx. 10 mm. Hg, to be 0·5 to 0·8% when drying *in vacuo* over P_2O_5 at 70° was used as a reference method.* A residual water content of the sample for p_{H2O} = 1 to 2·5 mm. Hg was accordingly estimated[57] at 0·05 to 0·2% for entrainment distillation with *iso*-octane, or 7 to 30 mg. for a 15-g. specimen.

In addition to the moisture which is not removed from the sample, all of that removed is not measured in the receiver. The water dissolved in the entrainer liquid in the receiver is readily estimated from solubility figures. For 20 ml. of *iso*-octane, this amounts to 7 mg. of moisture at 60°. The total water in the 40 ml. of liquid phase in the still was estimated[57] to be less than 0·2 mg. from vapour liquid phase equilibrium data for the water *iso*-octane system. In addition, water vapour diffuses out of the condenser during the distillation period. In the

*A residual water content of 0·5% is estimated for potato starch gel from Table I for p_{H2O} = 10 mm. Hg at 100°.

procedure of Mossel & Reith,[68] this water vapour is collected in a drying tube and measured. About 4 mg. of water were estimated to diffuse out of the condenser in a 5-h. distillation period, in good agreement with measured values in the absence of bumping. The total amount of water either not removed or not measured when steady-state conditions are reached in their entrainment distillation procedure with a 15-g. specimen was accordingly estimated at 15 to 37 mg. As an experimental check on these calculations, 12 determinations were made on 13-g. specimens of $BaCl_2.2H_2O$, which gave more reproducible results than water as a sample. On the average, 33 mg. less water was found than the theoretical amount. With four 6·5-g. specimens, the mean discrepancy was 30 mg. A correction of 0·03 ml. was accordingly adopted for their procedure. The observed discrepancies with $BaCl_2.2H_2O$ as the test material should be compared with an anticipated discrepancy of only 7 mg., since no sample residual moisture content is expected in this case. This would suggest a correction of 0·04 to 0·06 ml. as being more appropriate for determination of moisture in foods by this procedure.

Sair & Fetzer[66] found benzene distillation periods of more than 60 hours were required to reach a steady state in the removal of moisture from 40-mesh corn, a clear indication that diffusion of moisture within the material limits the rate of removal of water at low moisture levels in distillation procedures as it does in vacuum-drying methods. Overbeek & Mossel[57] confirmed this by showing that distillation periods required in practice are much greater than those estimated on the basis that p_{H2O} in the still is the vapour pressure of the specimen at its mean residual water content at all times during the distillation. Sample dispersion is accordingly just as important for distillation as for vacuum-drying procedures. The extraction of fats or oils by the entrainer may increase the moisture diffusivity of samples containing appreciable amounts of these.

Thermal degradation effects encountered in entrainment distillation are similar to those of vacuum-drying. When the amount of water collected continues to increase at a slow steady rate as the distillation time is greatly extended, degradation is indicated and choice of a lower-boiling entrainer should be considered. Agreement in moisture contents found with entrainers boiling at considerably different temperatures with no indications of degradation is evidence that the procedure may serve as a satisfactory reference method for such materials. As already mentioned, Sair & Fetzer[66] found that distillation with benzene (b.p. 80°) and toluene (b.p. 111°), and vacuum-drying at 38° and 50° all gave unequivocal results on corn which were in good agreement. The most rapid of these methods, toluene distillation, was accordingly accepted as a satisfactory reference method for corn. Similarly the results obtained with the *iso*-octane distillation procedure were found to show agreement within 0·1 to 0·2% moisture with those found by drying at 75° over P_2O_5 at less than 1 mm. Hg for potato starch, casein, wheat bran, bread crumbs and soya-bean flour.[61] These materials had moisture contents ranging from 8 to 19% and required distillation periods of 5 to 7 hours.

The importance of using suitable equipment and paying attention to pertinent detail in applying distillation procedures as reference methods has been stressed.[67,68]

Fischer volumetric method

The speed and high sensitivity of the Karl Fischer reagent for measuring moisture in a wide variety of materials have led to its increasingly widespread use despite its moderate instability.[71,72] Moisture in dehydrated food samples is made available for volumetric measurement by extraction with a suitable anhydrous solvent. Lack of residual moisture in the sample is accordingly dependent on the effectiveness of this solvent in making all the water available for titration. A comparison of the rates of removal of water in vacuum-drying methods with those indicated by Johnson's Fischer titration data[73] on through-40-mesh specimens shows that the rates of diffusion of moisture through dehydrated vegetables at 22° and at 60° is increased roughly 100-fold by soaking in methanol. This still required extraction times of one to several days at room temperature. The apparent water content varied with extraction time at 60° as shown in Fig. 8. Whereas carrots had apparently reached constant titres after extraction for ½ h., eggs, beets, onions, cabbage, peas and orange powder show slow but steady increases logically interpreted as due to thermal degradation or side reactions. The shapes of the curves for white and sweet potatoes, on the other hand, suggest that moisture has not all been removed after an extraction time of six hours at 60°. In other words, the situation is

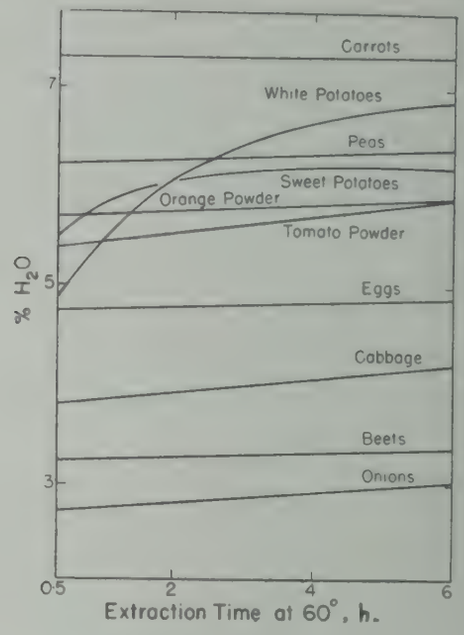


FIG. 8. *Fischer volumetric moisture values of dehydrated foods as a function of time of soaking in methanol at* 60°C
Data of Johnson.[73]

similar to that found for vacuum-drying where choice of conditions to minimize both drying time and undesirable side reactions means some sort of optimum compromise which may vary greatly for different materials.

Schroeder & Nair[74] compared three different procedures for Fischer moisture determinations of dried food products which are labelled (I), (II), and (III) here. (I) consisted of refluxing the sample in methanol for varying periods before titration. Neither (II) nor (III) involved heating and included suitable blanks. In (II), the titration was performed after the specimen had been in methanol for some designated period. In (III), titration of the water already extracted was repeated at intervals for each specimen. After initial periods of a day or so, the rate of extraction in (III) became practically zero for carrots and small but constant for cabbage, behaviour qualitatively similar to that in Fig. 8. Other materials also showed various constant rates of change under these conditions. On the other hand, constant maximum values were obtained in periods varying for different materials from a few hours to a few days by procedure (II) and, except for cabbage, these values agreed within 0·1% H_2O for those found by extrapolating to zero time the straight line portions of the drying curves found by (III). These values could then be used as a basis for choosing reflux times in (I).

Johnson[73] found no more than 0·03% moisture equivalent likely to arise from the presence of iodine-reducing substances in a variety of dehydrated foods. On the other hand, Schroeder & Nair[74] found a considerable increase in apparent water content when onion powder was left in methanol containing excess Fischer reagent. Ascorbic acid is known to react in the Fischer titration, but the amount present in dried foods is usually less than 0·1% moisture equivalent.[73]

McComb & McCready[75] found that formamide was much more efficient than methanol as an extraction solvent for moisture in dehydrated vegetables, probably because it acts as a solvent of plant carbohydrates.[76] Without the use of heat, the times required for extraction of moisture from through-40-mesh samples of carrots, sweet potatoes, peas and white potatoes were found to be respectively less than 3, 15, 60, and over 60 minutes. A mild, 40-second heat treatment to disperse the samples enabled unequivocal Fischer moisture contents to be obtained in each case in about 15 minutes. A later investigation[77] included a variety of dried food products. Those which were powders (eggs, garlic, onion, orange, tomato) required no heating to complete extraction of the water. Ten minutes in an air oven at 70° gave titres the same as for 50 minutes' heating time. Thus the use of formamide as an extraction solvent virtually eliminates thermal degradation as a possible source of error in Fischer determinations of moisture in dried foods.

Even where investigation shows that Fischer moisture values obtained using formamide are independent of extraction time, there still remains the unlikely possibility that a reproducible, small amount of Fischer reagent is rapidly consumed in a side reaction. Vacuum-oven moisture contents determined under conditions based on Makower's work were also obtained in the

formamide extraction studies.[75,77] For the four vegetables for which both Fischer and vacuum-oven moisture values corresponding to conditions determined by the redrying procedure are available, viz., onions, carrots, white potatoes and sweet potatoes, the moisture values found by the two methods usually agree within 0·2%, the range being 0 to 0·3% for a total of 11 samples investigated. This is nearly within the combined precisions of the two procedures, but it is probably significant that the higher value for each sample is the Fischer result. The conclusion seems justified that the evidence so far available indicates that the Fischer volumetric method with formamide as an extraction solvent furnishes a satisfactory basis for a reference procedure for determining the water content of dehydrated foodstuffs.

Nuclear magnetic resonance method

Nuclear magnetic resonance (NMR), discovered independently by Purcell and Bloch in 1946, involves transition between energy levels with the absorption or emission of electromagnetic radiation in the radio-frequency portion of the spectrum. The energy levels concerned are associated with the interaction of the magnetic moment of an atomic nucleus with an applied external magnetic field, H_0. In accordance with quantum mechanical principles, this interaction produces discrete energy levels in which the component of the nuclear magnetic moment along the applied field direction is quantized. Transition between one such level and the next higher one in energy is induced by superimposing, in a direction perpendicular to H_0, a weak magnetic field, H_1, the direction of which is reversed with a radio-frequency, ν, related to the difference in energy between the two levels, ΔE, by the Bohr frequency relation $\Delta E = h\nu$, where h is Planck's constant. For a given type nucleus, ΔE, and hence ν, depends on the magnitude of H_0, which is of the order of a few thousand gauss. Although many atomic nuclei possess magnetic moments, their magnetic resonance frequencies at a particular value of H_0 are quite different. Protons show NMR at frequencies about 21·29 megacycles per second for $H_0 = 5000$ gauss. This frequency corresponds to a wavelength of 14·09 m. and an energy of only 0·0200 cal./mole.

Shaw & Elsken[78] pioneered the application of NMR to measure water content of materials of biological origin and have explored the advantages and limitations of the method in a series of papers. The experimental arrangement[79] is indicated in Fig. 9. The permanent magnet is designed to produce a homogeneous field, H_0, in the region occupied by the sample contained in tube T. A current of a suitable fixed frequency (ν_0) is passed through the coil (r–f), which surrounds the sample tube and forms part of a highly tuned resonance circuit. A small current through the sweep coil (SC) is adjusted to vary H_0, and hence ΔE, over a range such that $\Delta E = h\nu_0$ is included.* Absorption of energy by the sample from the r–f coil is amplified, detected, and recorded on a strip chart instrument as a function of the sweep coil current. This record is a symmetrical band showing the amount of energy absorbed (A) in terms of the magnetic field (H_0). A is directly proportional to the number of protons in the sample.† Since there are advantages to working with the derivative, $D = \mathrm{d}A/\mathrm{d}H_0$, this quantity is usually recorded rather than A. Fig. 10 shows records both of A and of D *vs.* H_0 for water and for ice.[80] Provided band shape does not change, the maximum variation of D, labelled D_M, is proportional to A_M, the peak absorption. The difference in H_0 values for the maximum and minimum values of the derivative is called here the band width, w, and is usually expressed in frequency units corresponding to the associated change in ΔE. The significance of these terms is evident from Fig. 10.

Assuming that the records for water and ice in Fig. 10 are obtained under the same operating conditions on a single specimen, the absorption bands are found to have the same area. The difference in shape indicates that whereas the separation of the pertinent energy levels, ΔE, was very nearly the same for all the protons in the water sample, this was not true in ice. In other words, the protons in ice were subjected to a much wider range of effective magnetic field strengths than were those in water. In addition to the external field H_0, each proton is also subject to a weak internal magnetic field due to the nuclear moments of other protons and to electronic orbital moments. In liquid water, molecular rotation and random orientation effects result in a negligible net internal field for all the protons. In ice, where molecular orientation

*An alternative technique is to hold H_0 fixed and vary the r-f coil frequency.

†This assumes that H^1 is not large enough to alter significantly the normal distribution of population among the pertinent energy levels.

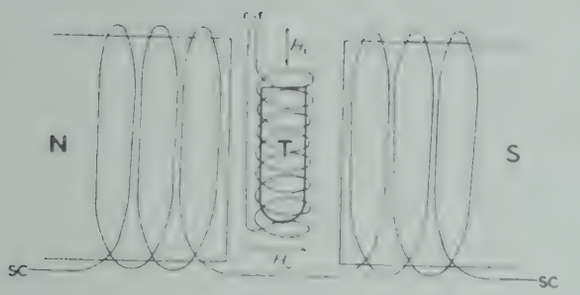


FIG. 9. *Schematic diagram of sample in position for NMR measurement*

Drawing is not to scale. The diameter of the pole faces is usually 6–10 in. The gap between pole faces is 1·5–2 in. SC is the sweep coil for varying H_0. Radio-frequency current through coil r-f produces alternating field H_0.

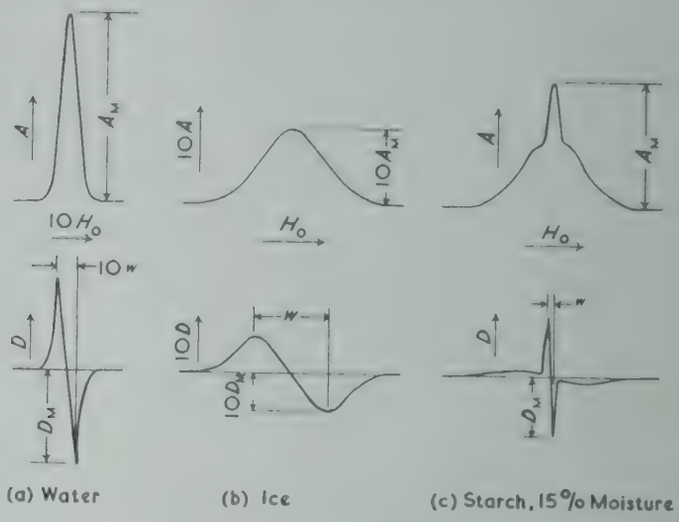


FIG. 10. *Appearance of NMR absorption records in terms of* A vs. H_0 *and of* D vs. H_0

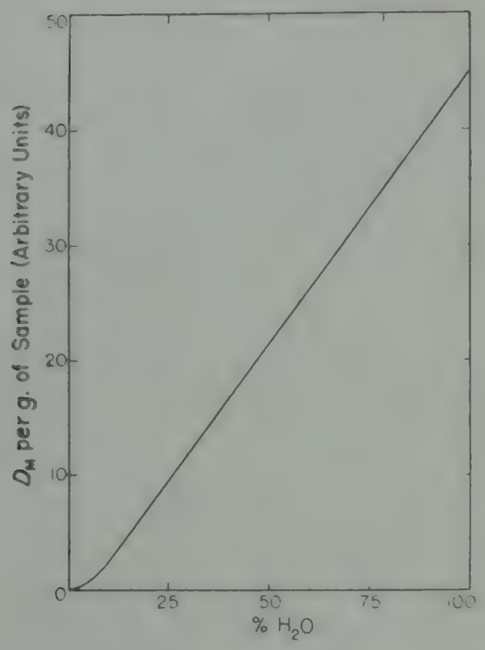
(*a*) Water, (*b*) ice, (*c*) starch containing 15% moisture. All curves are schematic. Approximate relative magnitudes are shown per g. of H_2O present. Note the indicated scale expansions.

is maintained more rigidly, this net internal field is not negligible, its magnitude and direction at any time varying sufficiently at different locations of the lattice to produce the observed broadening of the absorption band.

The behaviour of starch provides a typical illustration of how NMR absorption varies with water content in foodstuffs. The total absorption band may be thought of as the sum of three contributions. The first is weak absorption over a relatively broad frequency range due to H-nuclei in the dry material. This is present at all moisture levels as a more or less constant background over the narrower frequency region in which moisture absorbs. At low water contents, the band due to moisture is comparable in width and shape to that found in ice. As the moisture level increases, this band becomes stronger with the rate of increase of absorption being greatest at the centre of the band. Increase of moisture content above about 15% in starch causes increased absorption only in a very narrow region at the band centre. The absorption due to moisture above 15% resembles that found for an equivalent quantity of pure water. The band shape for starch containing about 15% moisture is shown in Fig. 10c. Fig. 11 shows the variation of D_M with moisture level. The curve was constructed from observations on starch powder[81, 82] in the 6 to 16% range and on aqueous suspensions of starch[83] for water contents above 60%. The standard deviation was about 2% for the high moisture range and about 0·2% for the low moisture range. Below about 6% water, D_M is too small to be measured reliably on the instrument employed.

The non-linear portion of the curve in Fig. 11 is the region in which the appearance of the absorption due to moisture is changing from a narrow to a broad band as the water is removed. The band width, w, can be used as a measure of water content in this range[81, 82] (Fig. 12) with the distinct advantage that neither the quantity nor homogeneity of the sample need be controlled. The increased band width reflects the limited mobility of the water sorbed at low moisture levels. The region in which this mobility changes rapidly as judged by NMR band widths is seen to be approximately the same as that indicated by sorption isotherm and other types of data.

Other materials investigated in the 5 to 20% moisture range with results similar to those for starch are pectin,[82] egg albumen[81] and potato granules.[84] Similarly, in the higher moisture range above 30% water, potato[78, 82, 85] and apple[78, 85] both show linear variation of D_M with water content. Reproducibility is particularly sensitive to sample homogeneity at higher moisture levels[85] due primarily to imperfect homogeneity of the external field H_0. It is in fact this non-homogeneity of field which determines the minimum band width observed for pure water in Fig. 12.



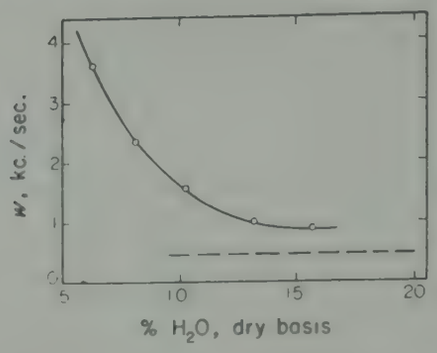


FIG. 11. (*left*) DM *per g. of sample as a function of water content of starch and starch suspensions*
Based on data of Shaw & Elsken.[81, 83]

FIG. 12. *Band width,* w, *as a function of water content of starch*
Data of Shaw & Elsken.[83] Broken line shows value of *w* for pure water.

Shaw & Elsken[83] showed that NMR absorption measurements can be carried out in such a way as to provide an absolute method for measuring water in the high moisture range in the case of starch. For the method to succeed, it is necessary that there be no non-aqueous components which have sufficient molecular mobility or flexibility to contribute to the narrow moisture absorption peak. Soluble solids in fresh apple tissue[85] and, in addition, fats in milk[86] were shown to interfere with application of NMR as an absolute moisture method.

To summarize, the NMR moisture method in its present state of development has the following advantages and limitations:

(1) Any moisture level above a few per cent can be measured, but the method is not absolute and the precision at high water contents is of the order of 1 or 2%.

(2) A precision of 0·1 to 0·2% can usually be realized in the 5 to 20% region, but the method is not applicable to very low moisture levels in foodstuffs.

(3) A determination can be made within a few minutes and does not require special skill on the part of the operator. A weighed sample having a volume not over 30 or 40 c.c. is used. Non-homogeneous materials may require some preparation of sample to obtain adequate precision at high moisture levels, but otherwise particle size and method of packing the sample are not critical.[84, 87]

(4) The sample is not destroyed. It can be in a sealed non-magnetic container. The method has been adapted for continuous-flow process control.[88]

(5) Soluble solids, fats, or oils present in a sample interfere with the method unless the contents of these components do not vary significantly on the dry basis.

(6) The equipment required is expensive. A commercial instrument is available[89] at a cost in excess of $10,000.

Continued development and application of NMR for measuring moisture contents can be expected to lead to improvements in precision and probably to reduction in the cost of commercial instruments. There are possibilities for making the method absolute which remain to be explored, but there seems to be little hope of extending the range to very low moisture levels.

Heat of dilution, dichromate oxidation method

Launer & Tomimatsu[90, 91] developed a rapid, convenient chemical method for the determination of moisture by measuring the non-aqueous content of a food sample based on the oxidation of organic matter by chromic acid. To a weighed specimen magnetically stirred in a measured volume of standard potassium dichromate solution is added a specified volume of concentrated sulphuric acid. The oxidation is practically complete in a few minutes at the elevated temperature produced by the heat of dilution of the acid. After a specified time, which can be as short as one minute, the mixture is diluted and the excess dichromate is electrometrically titrated with standard ferrous ammonium sulphate solution. The weight of dry sample per

equivalent of dichromate (F) is determined for each type of sample by use of a reference moisture method. This procedure was shown to yield results differing usually by only a few tenths per cent from those expected for complete oxidation of cellulose,[92] various carbohydrates,[93] and a number of organic acids, salts, and alcohols.[93]

Since an error of α% in measuring the solids content produces an error in percentage moisture content (W) of the sample of $(1 - W/100)\alpha$, the method is clearly best suited for relatively wet samples. Three factors may contribute to α, viz., reproducibility of the dichromate oxidation reactions, sampling errors, and applicability of the F value employed. The first of these is reflected in the variations observed in 10–12 replicate determinations of the amount of dichromate reduced per g. of specimen when the procedure is applied to relatively homogeneous materials. Standard deviations from the mean ranging from 0·09 to 0·13% were found for sucrose, glucose, and powders prepared from rice, dehydrated potatoes, and dehydrated peas.

Sampling error is reflected in higher variations in the dichromate equivalents found for less homogeneous samples. Materials which are not dry enough to be ground into a powder may be ground wet or blended with or without addition of water to form slurries from which the specimens are taken for analysis. The standard deviations from the mean found for specimens prepared in this way are 0·20% for prunes; 0·28–0·31% for fresh frozen corn, pineapple rice pudding and fresh frozen peas; and 0·45% for dehydrated potato cubes.

Variety, place of origin, crop year, maturity, size, method of preparation or processing, and storage history are among the factors which are expected to contribute to variations in the dichromate equivalent for a particular commodity. Standard deviations from the mean value of F found for a number of samples representing considerable variation in the pertinent factors just mentioned are listed in Table IV. Also shown are the mean water contents of these samples as determined by vacuum-oven reference methods with predrying in some cases. The accuracy of the dichromate oxidation method is indicated in the last column which shows the mean error in the moisture content resulting from calculating all values on the basis of the mean F value. All of the data of Table IV are from the papers already cited[90, 91] except those for lima beans.[94] Much of the large variation in F factor in this latter case was shown to arise from sampling error.

The range of dichromate equivalents for different foodstuffs is seen from Table IV to be rather limited. Higher values are found for foods rich in proteins or sugar and lower values are associated with high fat or oil content. The mean errors in moisture contents found in fresh peas and corn are not excessive despite their relatively high variation in F values. A mean error of only 0·09% would be expected for fresh potatoes of 78% water content on the basis of the relatively small variation found in F. Significant trends in F with maturity were noted for peas and lima beans, but they were in opposite directions.

Table IV

Accuracy of the dichromate oxidation method

Type of sample	Number of samples	Mean F, g. dry sample per equiv. dichromate	Standard deviation from mean F, %	Mean % H_2O (Reference method)	Mean absolute error, % H_2O (Dichromate method)
Potatoes, dehydrated	24	7·29	0·57	8·2	0·37
Peas, fresh frozen	14	7·48	2·22	78·1	0·43
Corn, fresh frozen	23	6·91	1·21	75·1	0·21
Prunes	42	7·53	0·75	17·4	0·50
Pineapple–rice pudding	26	7·26	0·44	67·6	0·10
Rice, white	10	6·89	0·41	11·8	0·31
Rice, brown	4	6·80	0·15	13·8	0·10
Rice, paddy	4	7·18	0·66	11·7	0·42
Rice, pre-cooked	9	6·83	0·51	*	0·14
Beans, lima	246	7·63	2·71	†	0·72

*Two samples below 10%; others from 47 to 74%.
†Range from 25 to 75%.

It is clear that the dichromate method is not to be recommended for low-moisture products in general, although there may be situations where the dispersion of F values likely to be encountered may be sufficiently low to make its use satisfactory. The method has the advantages that only 5 minutes or less are required to make a determination on a prepared sample, only

standard chemical equipment and readily available inexpensive electrical components are required, and good precision and accuracy are readily attained at higher moisture levels. It may also find applications where volatiles other than moisture are present or where materials are not conveniently analysed by single-stage oven methods.

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Discussion

Dr. J. R. Nicholls: The double-drying method depends on the assumption that, under the same temperature conditions, water mechanically added to the dried foodstuff is lost at the same rate as the water in the original foodstuff. Presumably if the assumption does not hold, the two curves will not be superimposable. Is this always so?

Dr. Stitt: In applying the redrying procedure as a reference method, it is verified that the initial drying curve and the drying curve of the rehumidified sample are superimposable at the temperature to be used in the routine procedure. If these curves are not superimposable, the drying temperature must be lowered to a value where this superimposability is obtained before the correct drying time can be determined using the redrying procedure as a reference method. I would modify your statement of the assumption on which the method is based to indicate that the losses of weight due to vaporization of water and to degradation reactions each occur at the same rate as a function of water content in the second drying as in the first.

Dr. B. P. Fish: Do the curves (Fig. 10c) for the N.M.R. spectrum of moist starch represent absorption by protons in the water molecules and not in the glucose residues? If so, can we suppose that the wide band represents proton signals from 'bound' water where the resonance absorption has been broadened by spin–lattice interaction; and that the narrow peak represents signals from 'free' water? This technique provides a further physical criterion to distinguish 'bound' and 'free' water.

Dr. Stitt: The curves of Fig. 10c represent the total absorption of all protons present, including those of the glucose residues in the starch. Most of the broad portion of the band arises from protons of the glucose residues. Mr. Elsken informs me that, on the instrument used, it was not feasible to measure the contribution of water protons to the broad portion of the band. The text of my paper perhaps gives the wrong impression on the broadness of the absorption band due to sorbent as compared with that due to firmly bound water. The proton-resonance band width for ice is of the same order of magnitude as that for dry starch. The study of band shape as a function of water content is one method of getting information on the binding of water from N.M.R. measurements. Another approach recently applied by Zimmerman[1] to silica gel involves measurement of the N.M.R. relaxation times T_1 and T_2 by the spin–echo method.

Prof. D. D. Eley: Would not the infra-red method yield valuable information on the nature and extent of bound water? This has been used by Russian writers[2] to identify physically adsorbed species on glass, and by Eischens[3] to identify chemically adsorbed species on nickel.

Dr. Stitt: Interesting information on the interaction of water with various sorbents might well be obtained from investigating the dependence on water content of the shape and intensity

of infra-red absorption bands, particularly those in the 3-μ region arising from OH stretching vibrations. The preparation of samples of sorbents of interest as components of foodstuffs in a suitable form for obtaining satisfactory infra-red absorption or reflectance spectra would be a major problem. High precision would also be required in such measurements because of the strong absorption arising from the presence of OH groups in the sorbent.

With regard to using infra-red absorption for measuring water content, direct measurement on solid samples of foodstuffs does not appear to be a feasible approach. The relative humidity of an atmosphere in equilibrium with the sample can be measured by infra-red absorption of the water vapour.[4] The water content of the sample could then be found if the water sorption isotherm of the material were known. Other methods of measuring R.H. would, however, be preferred for samples of foodstuffs.

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WATER-VAPOUR TRANSFER IN THE IN-PACKAGE DESICCATION OF DEHYDRATED FOODS

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A study of factors influencing the rate of in-package desiccation is reported, and an approximate equation for estimating rate of desiccation and effects of the individual components of the package is proposed. Transfer coefficients needed for this equation have been determined; comparisons show that estimated drying-time values are in reasonable agreement with those observed in model systems. The equation and the transfer coefficients can serve as guides for in-package desiccation design, particularly in estimating relative effects of variations in the individual components of the system.

Introduction

As previously reported,[1–4] non-enzymic browning and other deteriorative changes in certain dehydrated foods can be controlled by in-package desiccation. The process consists of packaging a product together with a desiccant held in a moisture-permeable container. Drying occurs during storage at warehouse temperature, and products can thus be dried, without scorching, to moisture levels substantially lower than those attainable by conventional methods. The process is employed commercially to protect quality and prevent caking in vacuum-dried fruit juice powders of the type developed by the Western Utilization Research and Development Division.[5] Military product descriptions and a specification cover the application of the method to juice powders[6] and to dehydrated vegetables.[7] Desiccant packaging, of which in-package desiccation is a special case, has aroused considerable interest as a means of maintaining satisfactory dryness in pharmaceuticals and in foods such as hard candies, crisp bakery goods, vitamins, and potato chips.[8–11]

Little quantitative information is available on factors controlling the rate of desiccation, and drying theory has not been developed for systems similar to in-package desiccation. In this paper an approximate equation for estimating the rate of desiccation and for estimating the relative effects of various components of the package is proposed. The analysis is not rigorous, but the correlation can serve as a guide where new or modified applications of in-package desiccation are contemplated.

Transfer coefficient data have been determined. In this work emphasis has been placed on effects of package atmosphere and of product, since earlier work[12] indicated that these components can control the rate of desiccation. A more detailed account of the present study is available elsewhere.[13]

Materials and analytical methods

The dehydrated vegetables used were produced by conventional methods. Two samples of most of them were used and are referred to as Lot 1 and Lot 2. The orange juice powder was produced by the vacuum puff-drying method.[5]

Moisture in the dehydrated vegetables was measured by the vacuum-oven method of Makower *et al.*[14] For orange juice powder the Johnson modification of the Karl Fischer method[15] was used. Vapour pressure was determined with Dubrovin gauges as modified by Legault *et al.*[16]

The calcium oxide used as desiccant for most of the work was an active recalcined hydrated lime. For part of the transfer-coefficient studies a lime produced by direct calcination of limestone was used.

Storage temperature was 34° with fluctuation of no more than ±1° in the small room in which transfer coefficients and model-system drying time values were determined, and no more than ±0·1° in the water-bath used for vapour-pressure measurements.

Theory

During in-package desiccation, water vapour must be desorbed, transferred, or absorbed

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by a series of package components, which are: the product (p), the package atmosphere (a), the desiccant container (c), and the desiccant (d), including any layer of hydrate.

The process is complex. Each package component offers some resistance to moisture transfer. The water vapour pressure and moisture content of the product change continuously during storage, as do the gradients through the package, but not in an easily defined manner. Because of this complexity it has not been possible to devise an exact relationship for calculating moisture content during desiccation.

An approximate relationship has been devised, however, which does permit estimation of the desiccation rate or of the time required for given moisture content reductions for model systems in which the desiccant covers one end of the desiccant container. The relation developed assumes a quasi-steady-state to exist for each of a series of moisture steps, and the estimate is made as a series of steps. Over a small moisture range the rate of desiccation $\Delta Q/\Delta\theta$ can be expressed as

$$\Delta Q/\Delta\theta = k_0 (p_p - p_d) A \quad \ldots\ldots (1)$$

where k_0 is the over-all transfer coefficient, p_p is the average water vapour pressure of the product, p_d is the vapour pressure at the interior of the desiccant (normally taken as zero), and A is the cross-sectional area of the model system. Consistent units are k_o, g. H_2O (day) (cm.^{2}) mm. Hg; p_p and p_d, mm. Hg; and A, cm.^{2}

For the assumed quasi-steady-state operation, water vapour is desorbed, transferred, or absorbed by each of the package components at a rate equal to the over-all rate of transfer $\Delta Q/\Delta\theta$. Equations similar to Equation (1) apply to each of the components:

For the product: $$\Delta Q/\Delta\theta = k_p (p_p - p_{pi}) W_p \quad \ldots\ldots (2)$$

For the package atmosphere: $$\Delta Q/\Delta\theta = k_a \left(\frac{p_{pi} - p_{ci}}{L_a}\right) A \quad \ldots\ldots (3)$$

For the desiccant container: $$\Delta Q/\Delta\theta = k_c (p_{ci} - p_{di}) A \quad \ldots\ldots (4)$$

For the desiccant: $$\Delta Q/\Delta\theta = k_d (p_{di} - p_d) A \quad \ldots\ldots (5)$$

p_p, the average vapour pressure of the product, is the value obtained on the ground equilibrated product, p_{pi} is the vapour pressure at the interface between the product and the package atmosphere, p_{ci} the vapour pressure at the interface between the package atmosphere and the desiccant container, p_{di} the vapour pressure at the desiccant container–desiccant interface, and p_d the vapour pressure at the interior of the desiccant. W_p is the weight of product, and L_a is the average transfer distance through the package atmosphere, equal to one-half the product depth. Because of differences in the nature of the package components the units of the individual transfer coefficients are not all the same. Consistent units are: k_p, g. (day) (g. product) mm. Hg; k_a, g./(day) (cm.^{2}), mm. Hg/cm.; and for k_c and k_d, g./(day) (cm.^{2}) mm. Hg.

From equations (1) to (5) it may be shown that:

$$\frac{1}{k_0 A} = \frac{1}{k_p W_p} + \frac{L_a}{k_a A} + \frac{1}{k_c A} + \frac{1}{k_d A} \quad \ldots\ldots (6)$$

Combining equations (1) and (6) gives the over-all rate of transfer in terms of the individual transfer coefficients:

$$\frac{\Delta Q}{\Delta\theta} = \frac{p_p - p_d}{\frac{1}{k_p W_p} + \frac{L_a}{k_a A} + \frac{1}{k_c A} + \frac{1}{k_d A}} \quad \ldots\ldots (7)$$

By applying equation (7) over successive moisture steps, the desiccation rate or the time required to remove a given amount of moisture from the product can be estimated. It will be noted from Table VI that in these estimates the over-all resistance usually changes rather slowly as the moisture content is reduced. Hence, rather large moisture steps can usually be taken without impairing the accuracy of the estimate.

It is sometimes convenient to represent the effects of the components as resistances. Thus:

$$\frac{\Delta Q}{\Delta\theta} = \frac{p_p - p_d}{r_p + r_a + r_c + r_d} = \frac{p_p - p_d}{r_0} \quad \ldots\ldots (8)$$

where r_0 is the over-all resistance $1/k_0A$, r_p is the resistance of the product $1/k_p W_p$, r_a is the resistance of the package atmosphere L_a/k_aA, r_c that of the desiccant container $1/k_cA$, and r_d that of the desiccant $1/k_dA$.

Limitations.—One limitation of the foregoing equations stems from use of the quasi-steady-state relation as the basis for calculation. Results show, however, that the over-all transfer coefficient changes relatively slowly during desiccation. Hence, errors from use of the quasi-steady-state relation are relatively small.

The principal limitation appears to be due to there not being taken into account the moisture and vapour pressure gradients that develop in the container in the direction of water vapour transfer. In the calculation it is assumed that the effective average water-vapour transfer distance is equal to half the product depth, but actually the effective transfer distance tends to be less than half the product depth in early stages of desiccation, and somewhat greater than half the product depth in later stages.

A third limitation may stem from the fact that the transfer coefficient for the drying piece, as here defined and determined, does not take into account the effect of the moisture gradient within the drying piece. As shown later, the product transfer coefficient falls rapidly with decreasing moisture content; this will be true for differential elements through the piece as well as for the piece as a whole. Hence, the average transfer coefficient, used in this study, will depend to some extent on the moisture gradient through the piece, and this in turn on the vapour pressure imposed at the surface of the piece by the other components of the package.

Despite these limitations, the agreement between observed and estimated drying-time values shows that the correlation can serve as a useful means of estimating rate of in-package desiccation and particularly the relative effects of the various components of the package.

Package atmosphere transfer coefficients

Package atmosphere transfer coefficients were determined in equipment which consisted of a lower chamber in which a saturated solution of sodium bromide was placed, a central chamber for the dehydrated product, and an upper container for the desiccant (magnesium perchlorate). The desiccant was supported by canvas which rested on $\frac{1}{4}$-in. screen soldered to the bottom of the desiccant container. The dehydrated product in the central chamber was supported by $\frac{1}{4}$-in. screen soldered to the bottom of the chamber. The entire apparatus was held in a moisture-proof container.

In operation, water vapour was transferred from the saturated sodium bromide solution, through the space between the solution and the dehydrated product, through the 'package atmosphere' around the product, through the canvas, finally to be absorbed by the magnesium perchlorate. The perchlorate was weighed periodically to determine the amount of water transferred. It was covered during the weighings to prevent absorption of moisture from the atmosphere. From the weight increase after a specified time and from the vapour pressure of the sodium bromide solution, the over-all resistance, r_0, of the system was calculated using equation (8). A control resistance, $r_{control}$, for all the components except the package atmosphere, was determined from weight increases of the perchlorate container when placed directly on the sodium bromide solution container with a 1-cm. air space between the solution and the lower part of the desiccant container. From these resistances the resistance of the package atmosphere was determined:

$$r_a = r_o - r_{control}$$

From r_a the transfer coefficient k_a of the package atmosphere was calculated ($r_a = L_a/k_aA$).

The weight of the magnesium perchlorate in the desiccant container was 2 g. cm.^{2} To avoid a falling rate of absorption due to the presence of an increasingly thick layer of hydrate through which the water vapour would have to be transmitted, the perchlorate was periodically replaced when only partially hydrated.

Because of the possibility that the rate of moisture transfer might be significantly affected by an initial moisture absorption or desorption by the dehydrated products, the transfer was continued long enough to establish that a steady state had been reached. Graphs of the data for white potato, carrot and cabbage as well as the control are all straight lines, showing that the transfer was not affected by absorption or desorption of moisture by the vegetable samples in the early stages of the experiment.

The vapour pressure over saturated solutions of sodium bromide at 34·0° was measured as 21·9 mm. of mercury. The transfer coefficient values obtained are in Table I. It is of interest to compare observed values of k_a with those calculated assuming steady-state diffusion[17] through the package atmosphere. If the cross-sectional area perpendicular to the direction of diffusion is taken to be the cross-section of the desiccant container multiplied by the void fraction of the solids, and if the water vapour pressure is negligible relative to the total pressure, the following equation applies:

$$k_a = \frac{86{,}400}{760} \cdot \frac{DM_w \varepsilon}{RT} \qquad (9)$$

where: R = gas constant, c.c.-atm./mole-°K,
T = temperature, °K,
M_w = molecular weight of water vapour.
ε = void fraction of solids, and
D = diffusion coefficient of water vapour through air, cm.²/sec.

Table I compares values of k_a from equation (9) with experimental results for the white potato, carrot and cabbage systems. In view of the circuitous path the water vapour must travel in diffusing through the air surrounding the product pieces, it appears reasonable that the calculated transfer coefficients should be greater than those measured. Although equation (9) therefore cannot be used for direct estimation of k_a, the relationship may be useful for prediction of the effect of temperature on k_a.

Table I

Transfer coefficients for the transfer of water vapour through the atmosphere (air) within packages of dehydrated white potato, carrot and cabbage

Product*	Bulk density, g./ml.	Absolute† density, g./ml.	Fraction voids between product pieces	Transfer coefficients** Experimental	Transfer coefficients** Calculated††
White potato	0·38	1·45	0·74	$0{\cdot}012_4$	0·0162
Carrot	0·38	1·46	0·74	$0{\cdot}011_1$	0·0162
Cabbage	0·24	1·41	0·83	$0{\cdot}008_4$	0·0182

*Carrot and white potato were of $\frac{3}{8} \times \frac{3}{8} \times \frac{3}{16}$ in. size before dehydration; cabbage was $\frac{1}{8}$ in. shreds; all were Lot 2 materials.

†Absolute density was determined by benzene displacement.

**g. of H_2O/(day) (cm.²) mm. Hg/cm. Based on the over-all cross-section of the container.

††Using D for water vapour of 0·270 cm.²/sec. at 34°.[20]

Desiccant and desiccant container transfer coefficients

Transfer coefficients for two active lime samples and for three potential desiccant container materials were determined at water vapour pressures of 1·1 and 4·3 mm. of mercury. Two vapour pressures were used in order to determine whether the transfer coefficients of these components are affected significantly by vapour pressure at the low humidities prevailing during in-package desiccation. Considerable variation seemed possible. Studies by Doty *et al.*[18] have shown that for some hydrophilic membranes at certain relative humidities there is an abrupt drop in permeability with decreasing humidity, and approximate diffusion calculations by Van Arsdel[19] for the falling-rate phase of drying have shown that the rapid fall in drying rate of dehydrated vegetables with decreasing moisture content can be ascribed to decreasing diffusivity.

Method

In this study 250-mm. desiccators with heavy wire screens for plates were used. Diffusional resistance of the air was eliminated by a fan rotating inside a vertical cylinder attached to the wire screen, the fan motor and bearings being externally connected to avoid vibrating the desiccator. The fan shaft was a loose fit in lubricated rubber tubing connected to the metal sleeve through which the shaft passed into the desiccator. To ensure that the lubricant would not be thrown on to the samples, a second cylinder was provided extending from the rubber stopper in the top of the desiccator, to below the top of the cylinder in which the fan rotated. The solutions used to maintain the desired humidities were saturated solutions of lithium

chloride, or sulphuric acid solutions maintained at 72·9–73·7% acid. The vapour pressure of these solutions at 34° were estimated from International Critical Tables data[20] as 4·3 and 1·1 mm. of mercury, respectively; observed vapour pressures were $4{\cdot}3_7$ and $1{\cdot}0_9$ mm. of mercury at 34·0° for saturated lithium chloride and 73·1% sulphuric acid solutions, respectively.

The lime samples and the desiccant-container materials were held in containers similar to those used for the Technical Association of the Pulp and Paper Industry permeability tests.[21] For the lime samples, which were powdered to improve uniformity, parallel runs were made with container loads of two depths, 0·42 and 1·68 g./cm.^{2}. For the desiccant-container materials, 0·42 g./cm.^{2} of Lime H (recalcined hydrated lime) was placed in each sample holder, a disc of the container material was sealed in place using the TAPPI template and hot wax procedure, and the sample holder was inverted to eliminate the layer of air between the desiccant and the moisture-permeable barrier. All tests were performed in duplicate. The samples were weighed periodically during hydration. The hydration curves in Fig. 1 are typical of those obtained.

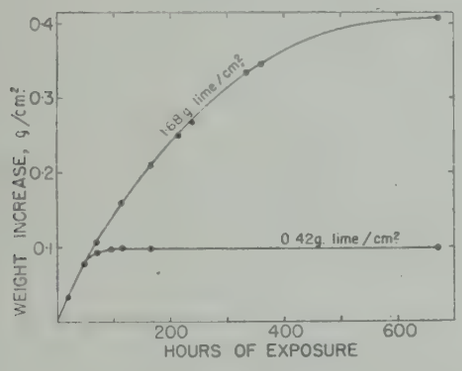

FIG. 1

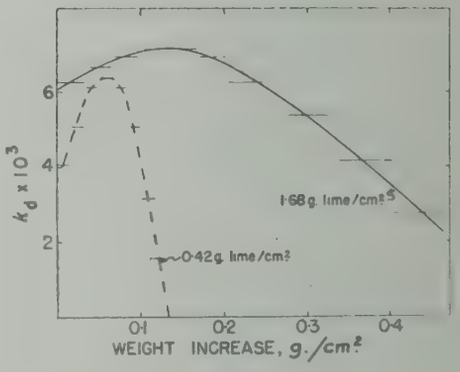

FIG. 2

FIG. 1. *Hydration of recalcined Lime H over saturated lithium chloride solution at* 34°C

FIG. 2. *Transfer coefficients g./(day) (cm.^{2}) (mm. Hg) of Lime A (calcined limestone) at* 34° *and* 4·3 *mm. Hg (calculated)*

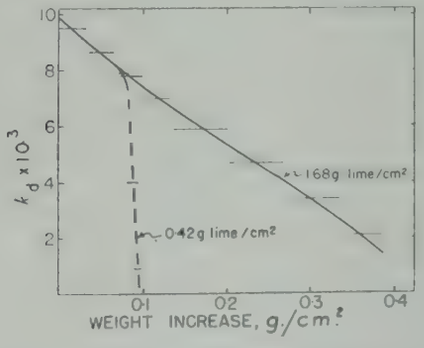

FIG. 3. *Transfer coefficients g./(day) (cm.^{2}) (mm. Hg) of recalcined Lime H at* 34° *and* 4·3 *mm. Hg.* (Calculated from the data in Fig. 1)

Results on desiccant

Transfer coefficients for various segments of the hydration curve, calculated by equation (7), are shown in Figs. 2 and 3. The relation between the transfer coefficient and the degree of hydration is seen to be complex; it appears to reflect the history of the lime. Thus a maximum is apparent in the curves for the calcined limestone (Fig. 2). This maximum, indicative of an induction period, has been observed with other samples of calcined limestones but not with any of the samples of recalcined hydrated lime which have been studied.

The decrease in transfer coefficient as desiccation proceeds can be ascribed in part to resistance of the layer of hydrated lime which is formed, and in part to depletion of the lime sample. The latter influence becomes significant as the process approaches completion. The difference in the heights of the curves in Fig. 2 indicates that for Lime A the reactive absorbing

layer was relatively diffuse, i.e., that the depth of the absorbing layer was greater than that of the 0·42 g. cm.^{2} sample. In contrast, Fig. 3 shows that for Lime H the rate of water vapour absorption was not dependent on the quantity of desiccant per unit area in the range studied.

The effect of vapour pressure on the transfer coefficient is shown in Table II. The rough correspondence in the values observed for paired samples hydrated at vapour pressures of 1·1 and 4·3 mm. Hg indicates that the transfer coefficient is sensibly independent of vapour pressure in the range studied. Later in this paper, it will be shown that differences such as that found for one of the paired samples for Lime H will have little effect on the calculated desiccation rate when all elements of the in-package desiccation unit are taken into account.

Table II

Average transfer coefficient k_d* *for samples of lime at 34° and vapour pressures of 1·1 and 4·3 mm. of mercury, over range of 0–16% weight increase*

Sample	Weight of lime, g./cm.^{2}	Weight increase, g./cm.^{2}	$k_d \times 10^3$ 1·1 mm.	$k_d \times 10^3$ 4·3 mm.
Lime A	0·42	0·068	4·2	5·2
,,	1·68	0·270	6·5	6·7
Lime H	0·42	0·068	13·0	9·0
,,	1·68	0·270	6·8	6·4

*k_d: g./(day) (cm.^{2}) (mm. Hg).

Results on desiccant container

The three desiccant-container materials tested were 18-oz. canvas, laminated chip board of 2·0 mm. thickness, and corrugated wood pulp of 1·7 mm. maximum thickness. The transfer coefficients of the desiccant-container materials were calculated from the lengths of time required for 16% weight increase of the lime above the container materials using equation (7) to calculate k_c, the values of k_d being known from the rate of moisture absorption of the lime samples which were open to the desiccator atmospheres. The data are in Table III. As was found with the lime samples, the transfer coefficients obtained for these desiccant-container materials are essentially independent of the vapour pressure over the range studied.

Table III

Transfer coefficients k_c* *for samples of desiccant-container materials at 34° at vapour pressures of 1·1 and 4·3 mm. of mercury*

Sample	$k_c \times 10^3$ 1·1 mm.	$k_c \times 10^3$ 4·3 mm.
Laminated chip board	4·3	4·0
Corrugated wood pulp	3·6	3·4
Canvas (18 oz.)	~60	~70

*k_c: g./(day) (cm.^{2}) (mm. Hg).

Product transfer coefficients

Determination of the product-transfer coefficients was carried out as follows:

Following preparation, the dehydrated vegetables (Lot 1) were stored at room temperature in closed containers for 48 hours. Each lot was then divided into five 50-g. samples which were placed in tared metal weighing dishes, weighed, and placed in desiccators over lime for desorption. The five desiccators, with attached vapour pressure apparatus,[16] were evacuated and held at 34°. Total pressures below 0·1 mm. of mercury were maintained in the desiccators throughout the experiment. Experimental conditions corresponded to essentially zero partial pressure of water vapour at the surface of the solid. Samples were removed periodically, weighed, and changes in moisture content computed from the weight loss. After removal, each sample was ground and its vapour pressure at 34·0° determined. Moisture content and vapour pressure data are recorded in Table IV.

Table IV

Transfer coefficients, equilibrium vapour pressures and moisture contents of dehydrated vegetables desorbed at 34°
(Total pressure at exterior of vegetable pieces during desorption, < 0·1 mm. of mercury)

Vegetable	Desorption time (cumulative), days	Moisture content range,* %	Vapour pressure range,† mm. Hg	Average over moisture range**, $k_p \times 10^5$
White potato, Lot 1	0·31	8·3–6·7	15·0– 8·5	460
	1·01	6·7–5·6	8·5– 4·7	230
$\frac{3}{8}$ in. × $\frac{3}{8}$ in. × $\frac{3}{16}$ in.	2·08	5·6–4·0	4·7– 3·1	190
	13·3	4·0–2·4	3·1– 1·3	70
	84	2·4–1·0	1·3– 0·2	26
Cabbage, Lot 1	0·14	3·0–2·7	9·1– 8·0	250
	0·96	2·7–2·4	8·0– 6·9	49
$\frac{1}{8}$ in. Shreds	14·3	2·4–1·5	6·9– 4·9	11
	40	1·5–0·7	4·9– 3·4	9
	84	0·7–0·3	3·4– 2·2	4
Carrot, Lot 1	4·0	9·0–6·7	15·8–12·6	41
	14·0	6·7–5·6	12·6–10·3	10
$\frac{3}{8}$ in. × $\frac{3}{8}$ in. × $\frac{3}{8}$ in.	76	5·6–3·7	10·3– 7·6	3
Carrot, Lot 1	3·25	9·0–7·0	16·0–12·5	44
	14·0	7·0–5·5	12·5– 9·9	13
$\frac{3}{8}$ in. × $\frac{3}{8}$ in. × $\frac{3}{16}$ in.	76	5·5–3·7	9·9– 6·8	4
Carrot, Lot 1	1·4	7·4–6·3	12·2–10·4	70
	4·0	6·3–5·4	10·4– 9·8	41
$\frac{3}{8}$ in. × $\frac{3}{8}$ in. × $\frac{1}{16}$ in.	25	5·4–3·8	9·8– 6·9	9
	76	3·8–2·6	6·9– 4·6	4

*Moisture-free basis. Determination by method of Makower *et al.*[14]
†Equilibrium vapour pressures, determined on equilibrated ground samples.
**(g. H_2O)/(day) (g. product) (mm. Hg.).

The average transfer coefficient, k_p (Table IV), was then calculated using equation (7) for each of the successive moisture steps in the experiment. For these calculations, the values of $p_p - p_{pi}$ used for the various moisture steps were the average equilibrium vapour pressures for these moisture steps. It will be noticed that in the calculation of k_p, $p_p - p_{pi}$ was taken, not as the maximum vapour pressure difference existing within the piece, but as the difference between the vapour pressure at the exterior of the piece during dehydration, and the vapour pressure after grinding and equilibrating. This procedure was followed because the equilibrium vapour pressure can be determined much more reliably than can the maximum vapour pressure.

Fig. 4 shows the transfer coefficients obtained for the desorption of moisture from the dehydrated vegetable samples and shows that these transfer coefficients fall markedly as the moisture content is reduced. For the cabbage, k_p fell from 0·00250 to 0·00004 g. H_2O/(day)

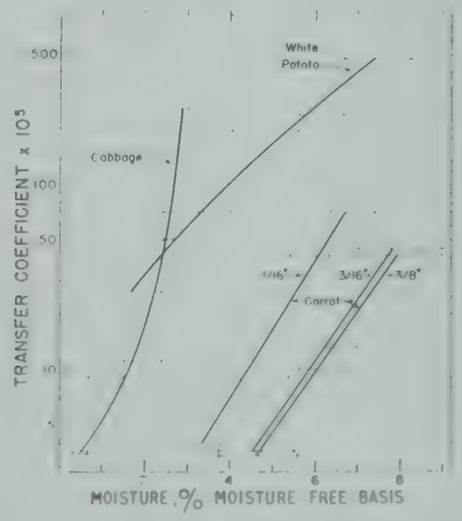

FIG. 4. *Transfer coefficients g./(day) (g. product) (mm. Hg) at 34° for dehydrated products, as a function of product moisture content*

(g. product) (mm. Hg) as the moisture content was reduced from 2·9 to 0·5%. Decreasing the thickness of the pieces of the carrot samples increased the transfer coefficients, the values at comparable moisture levels for the samples of $\frac{3}{8}$, $\frac{3}{16}$, and $\frac{1}{16}$ in. nominal thickness being in the ratio of approximately 1 : 1·1 : 4. Variation of k_p would be expected as a result of increased diffusional resistance with increase in piece thickness.

Observed and estimated drying time values

To obtain experimental data for comparison with estimated drying-time values (below), and to obtain a direct check on the improvement in rate of desiccation attainable by reducing the transfer distance through the package atmosphere, in-package desiccation tests were conducted using model systems consisting of containers (10 cm. dia.) for the material above which was placed a receptacle containing calcium oxide covered with canvas.

The depths of the dehydrated products in the various containers were respectively 7·5, 15, and 30 cm. To prevent moisture absorption from the surrounding atmosphere the model systems were held in moisture-proof containers. The dehydrated foods were adjusted to approximately Armed Forces specification moisture levels[22] prior to beginning of the desiccation, and the moisture ranges included were approximately those that would be covered during the in-package desiccation of these products. Moisture removal was followed by periodic weighing of calcium oxide containers. The residual moisture contents, calculated from the initial moisture contents and from the weight increases of the desiccant, were then plotted against the storage time. From these plots the lengths of time for given moisture reductions were read; the drying-time values so obtained are listed in Table V.

Table V

Observed and estimated days for desiccation of dehydrated foods in model systems
(Depths of products, 7½, 15 and 30 cm.)

Commodity	Moisture range,%*	Days for given moisture reduction for container of given depth					
		Observed			Estimated		
		7½ cm.	15 cm.	30 cm.	7½ cm.	15 cm.	30 cm.
Cabbage	4·0–3·0	1·5	3·2	8·4	1·1	3·7	13·8
⅛ in. shreds	4·0–2·0	6·5	13·2	25	5·6	12	35
(Lot 2)	4·0–1·0	32	57	83	34	46	90
White potato	9·5–8·5	0·7	1·5	4·0	0·8	2·5	9·4
⅜ in. × ⅜ in. × $\frac{3}{16}$ in.	9·5–7·5	1·7	4·6	13·2	1·8	5·8	22
(Lot 2)	9·5–6·5	3·4	9·6	28	3·2	10·3	38
	9·5–6·0	5·2	13·6	39	4·4	13·8	50
Carrot	7·1–6·1	2·8	4·5	—	5·5	7·9	
⅜ in. × ⅜ in. × $\frac{3}{16}$ in.	7·1–5·1	13	20	—	17	22	
(Lot 2B)	7·1–4·1	47	65	—	48	57	—
Carrot	7·0–6·0	1·0	2·5	6·5	—	—	
⅜ in. × ⅜ in. × $\frac{1}{16}$ in.	7·0–5·0	4·0	8·6	20	—	—	—
(Lot 2C)	7·0–4·0	13	28	42	—	—	—
Onion	3·9–2·9	2·4	6·0	16	—	—	—
flakes	3·9–1·9	10	24	59	—	—	—
	3·9–0·9	40	97	170	—	—	—
Potato	7·2–6·2	1·8	6·0	—	—	—	—
granules	7·2–5·2	6·2	23	—	—	—	—
	7·2–4·2	15	52	—	—	—	—
Orange	2·7–1·7	7·0	18	—	—	—	—
powder	2·7–0·7	41	76	—	—	—	—

*Moisture-free basis.

Vapour-pressure isotherms were then determined for portions of the white potato, cabbage, and carrot (Fig. 5).

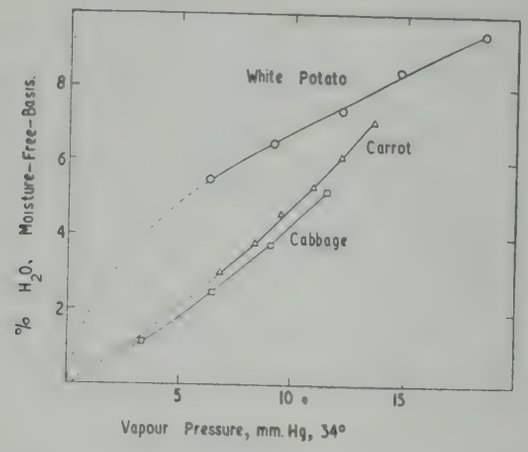

FIG. 5. *Water vapour pressure isotherms of Lot 2 dehydrated white potato, carrot, and cabbage*

Estimated drying time

With these vapour-pressure data, together with transfer-coefficient data given above, the lengths of time required for given moisture reductions of the dehydrated white potato, cabbage, and carrot in the 7·5-, 15- and 30-cm. containers were then estimated, using equation (7).

The drying time values so estimated are listed in Table V. Comparison with the observed values indicates the agreement to be satisfactory. The principal differences on a percentage basis are for the early part of the desiccation; these differences are relatively unimportant because of the small number of days involved.

Confirming previous indications[12] regarding effects of product depth, the data in Table V show that product depth does have a marked effect on rate of desiccation. Drying-time values observed for the 30-cm. containers range from 3 to 7 times as long as those for the 7·5-cm. containers. For pieces of carrot $\frac{3}{8} \times \frac{3}{8} \times \frac{3}{16}$ in., the product depth had less effect than for the other products, as would be expected when the resistance of the product begins to predominate.

Effects of individual components

Table VI shows estimated resistance values for the various individual package components, for the white potato, cabbage, and carrot in the 15-cm. containers. The data show that the resistance of the package atmosphere was substantial. Neither the desiccant nor the desiccant container (canvas) offered large resistance. For the product itself, the resistance varied widely with the product and with its moisture content. For white potato, the product resistance was low over the entire moisture range considered, for cabbage it was low at the initial moisture content but became very high at the end of desiccation, and for $\frac{3}{8} \times \frac{3}{8} \times \frac{3}{16}$-in. carrot it was high even at the beginning of desiccation.

From equation (7) it can be shown[13] that, if the sole resistance were that of the package atmosphere, the length of time for a given degree of drying would vary with the *square* of the product depth; but that if the product offered the only resistance, the rate of drying would be *independent* of product depth. Hence, for products such as dehydrated white potato, which offer little resistance of their own, the drying rate could be made as rapid as desired by reducing product depth.

For products such as the $\frac{3}{8} \times \frac{3}{8} \times \frac{3}{16}$-in. carrot, however, which themselves offer large resistance, reducing the product depth below a certain point would have little effect on the over-all resistance, and hence little effect on the drying rate. If more rapid drying were desired, other measures, such as reducing the thickness of the drying piece, would be necessary. The date in Table V show that reducing the thickness of the carrot did substantially reduce the drying time, the observed drying-time values for the samples of $\frac{1}{16}$-in. thickness being only about 30 to 40% of the corresponding values for samples of $\frac{3}{16}$-in. thickness.

Summary and conclusions

An equation for estimating the rate of in-package desiccation and for studying the effects of the individual package components on the rate of desiccation has been developed

Table VI

Resistance of individual package components to moisture transfer during the in-package desiccation of dehydrated white potato, cabbage and carrot at 34°, in model systems for product depths of 15 cm. and for given changes in moisture content

Individual component	Resistance of individual package component*								
	White potato $\frac{3}{8}$ in. × $\frac{3}{8}$ in. × $\frac{3}{16}$ in.			Cabbage $\frac{1}{8}$ in. shreds			Carrot $\frac{3}{8}$ in. × $\frac{3}{8}$ in. × $\frac{3}{16}$ in.		
	9·5 to 8·5% H_2O	8·5 to 7·5% H_2O	7·5 to 6·5% H_2O	4·0 to 3·0% H_2O	3·0 to 2·0% H_2O	2·0 to 1·0% H_2O	7·1 to 6·1% H_2O	6·1 to 5·1% H_2O	5·1 to 4·1% H_2O
Product†	0·27	0·36	0·55	0·4	8·3	46	14	26·5	65
Atmosphere**	7·7	7·7	7·7	11·4	11·4	11·4	8·6	8·6	8·6
Desiccant container††	0·20	0·20	0·20	0·20	0·20	0·20	0·20	0·20	0·20
Desiccant§	1·41	1·60	2·12	1·4	1·5	1·7	1·3	1·5	1·6

*(mm. Hg) (day) (cm.²)/(g. H_2O).

†Product: $r_p = 1\ k_o W_p$; k_p from Fig. 4. Weight of product, moisture-free basis: 457 g. for white potato; 241 g. for cabbage; and 444 g. for carrot.

**Atmosphere of package: $r_a = L_a/k_a A$. Data from Table I.

††Desiccant container, canvas. $r_c = 1/k_c A$. $k_c = 0{\cdot}065$ g./(day) (mm. Hg) (cm.²).

§Desiccant: $r_d = 1/k_d A$. Data from Fig. 3.

Estimated and observed drying-time values are in reasonable agreement, indicating that the method can serve as a guide for design of in-package desiccation systems, particularly in determining the relative effect of the various package components.

Transfer coefficients needed for use in this equation have been determined for materials representative of each of the package components.

Transfer coefficient values determined for the package atmosphere (air–water vapour) in containers of dehydrated white potato, carrot, and cabbage at 34° were, respectively, $0{\cdot}012_4$, $0{\cdot}011_1$, and $0{\cdot}008_4$ g./(day) (cm.²) (mm. Hg/cm.).

For the desorption of water vapour from the dehydrated vegetables, the transfer coefficients fall markedly with decreasing moisture content. For cabbage, the coefficient fell from 0·00250 to 0·00004 g. (day) (g. product) (mm. Hg) as the moisture content was reduced from 2·9 to 0·5%. Reducing the piece thickness of the dehydrated carrot increases the transfer coefficient, values for samples of $\frac{3}{8}$-, $\frac{3}{16}$-, and $\frac{1}{16}$-in. thickness being in the ratio of ~1 : 1·1 : 4.

Transfer coefficients determined for two active calcium oxide samples and for three desiccant-container materials were all approximately independent of vapour pressure at the low vapour pressures used (1·1 and 4·3 mm. of mercury at 34°).

Estimated and observed drying-time values show there is a pronounced decrease in rate of desiccation with increase in transfer distance through the product atmosphere, observed drying-time values ranging from three to seven times as long in containers of 30 cm. depth as in those of 7·5 cm. depth.

The estimates show that the package atmosphere offered a substantial resistance to water vapour transfer in containers 15 cm. in depth. Neither the desiccant nor the desiccant container (canvas) offered a large resistance under the conditions of these experiments. The resistance of the product varied markedly with the type of product and with its moisture content. For white potato, this resistance was small over the entire moisture range considered, for cabbage it was low at the beginning of desiccation but became very high at the end of desiccation, and for carrot ($\frac{3}{8}$ × $\frac{3}{8}$ × $\frac{3}{16}$-in.), the resistance was high even at the beginning of desiccation.

Acknowledgment

The authors are pleased to acknowledge the suggestions and interest of M. A. Joslyn of the Department of Food Technology, University of California.

Nomenclature

Symbol	*Definition*	*Units*
A	= Area	cm.^{2}
D	= Diffusion coefficient	cm.^{2}/sec.
k_a	= Transfer coefficient, package atmosphere	(g. H_2O) (day) (cm.^{2}) (mm. Hg/cm.)
k_c	= Transfer coefficient, desiccant container	(g. H_2O) (day) (cm.^{2}) (mm. Hg)
k_d	= Transfer coefficient, desiccant	(g. H_2O)/(day) (cm.^{2}) (mm. Hg)
k_p	= Transfer coefficient, product	(g. H_2O) (day) (g. product) (mm. Hg)
L_a	= Transfer distance through the package atmosphere in a straight line in the direction of transfer	cm.
M_w	= Molecular weight	g./mole
P	= Total pressure	atm.
p	= Water vapour pressure	mm. Hg.
Q	= Quantity of water vapour transferred	g.
R	= Gas constant	(cm.^{3}) (atm.)/(g.-mole) (°K)
r	= Resistance to water vapour transfer	(mm. Hg) (day) (cm.^{2})/(g. H_2O)
T	= Temperature	°K
W_p	= Weight of product	g.
ε	= Void fraction	
θ	= Time	days

Subscripts

a = Package atmosphere
c = Desiccant container
d = Desiccant
p = Product
pi = Product–atmosphere interface
ci = Desiccant container–atmosphere interface
di = Desiccant–desiccant container interface

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Discussion

Mr. E. G. B. Gooding: In-package dessication was tried experimentally in the U.K. about 1944, but the space occupied by the desiccant was so large that the procedure seemed to be impracticable. The matter is now being re-investigated and seems far more promising. The reason is that with current drying techniques and specifications, the moisture content of the product is much lower than during World War II. Consequently, less moisture has to be removed from the dehydrated food by the desiccant to bring the moisture content of the product to whatever low level is required. In practice, with potatoes of 5–6% moisture content, a sacrifice of only about 10% of the space in the can is required for the desiccant container if the moisture content is to be brought to about 3·5%, and with cabbage a sacrifice of 3% or so of the space. The result is about a three-fold increase in tropical storage life.

Mr. J. F. Hearne: When lime is used as a desiccant, bridging across the lime container may occur. Does this markedly reduce the rate of water transfer? When using cylindrical containers, I have noticed that bridging is least when the height of the container does not exceed the diameter. Has Dr. Burr any views on desirable shape and construction of containers for desiccants?

Dr. Burr: We have no information on the influence of bridging of the lime on the rate of water vapour transfer through it. Dr. Hendel has also found bridging less serious in relatively shallow containers. In recent years we have abandoned the use of rigid desiccant containers in favour of bags made from a heat-sealable, stretchable, X-creped kraft paper. This type of packet offers some savings in space and cost and, if properly designed, eliminates the problem of containers rupturing through expansion of the lime. It has been used with commercial fruit powders in the United States for a number of years and is reported to be very satisfactory.

Mr. E. J. Rolfe: Does Table V refer to work carried out at 34° as reported in the remaining tables? Do you have any information on the temperature coefficient of desorption using lime as an in-package desiccant?

Dr. Burr: The data of Table V are for 34°. The temperature coefficient of in-package desiccation with lime appears to be about 2 to 3 per 10°C, considerably smaller than the coefficients of non-enzymic browning and of caking. If a product may encounter high temperatures in transportation or storage, it is probably wise for the processor to hold the packaged material for a time in order that partial desiccation will take place before it leaves his hands. The greatest transfer of moisture will occur during this period if the product is held at the highest temperature at which neither browning nor caking will be appreciable. In many practical cases this optimum temperature will probably be in the neighbourhood of 30–35° or higher, but it would have to be determined experimentally for any given system.

Mr. Joyce: Dr. Burr has mentioned the use of temperatures in the neighbourhood of 37° for short periods for permitting rapid in-can desiccation of fruit juice powder. It has been our experience that in mixtures of fruit juice and sugars at this temperature, considerable changes take place in the crystalline structure of the sugar, and I would like to ask Dr. Burr if he has found this phenomenon in his powders.

Dr. Burr: We encounter more or less severe caking of our fruit powders if they are placed at too high a temperature when first packaged. For example, with orange powder at an initial moisture level of 2·8%, packed with lime in 6-oz. cans and immediately placed in storage at 100°F (38°C), moderate caking was observed. No caking occurred if the cans were stored at 90°F (32°C). No other changes in crystalline structure have been noticed.

SESSION IV

Chairman : Prof. A. W. Scott

A STUDY OF EVAPORATION AND DIFFUSION PROCESSES IN THE DRYING OF FISH MUSCLE

By A. C. JASON

(*Torry Research Station, Aberdeen*)

The rate of drying of fish muscle during the constant-rate period is controlled solely by the conditions of the ambient atmosphere and is equal to that from a saturated surface of the same shape. The duration of the constant-rate period is related to the rate of evaporation per unit area by an expression involving the effective diffusion constant, the thickness of the sample and the free water concentration as parameters.

Drying during the falling-rate period takes place in two distinct phases, in each of which the behaviour is in accord with a solution of the diffusion equation based on Fick's Law. In each phase, drying is characterized by an effective diffusion coefficient which is independent of shrinkage of the muscle and which in the first phase is considerably greater than in the second phase. Both coefficients vary with temperature according to an Arrhenius type of equation in which the energy of activation for diffusion is one of the parameters. The transition from the first to the second phase appears to be associated with the uncovering of the unimolecular layer of water which covers the protein molecules. Experimental evidence suggests that the processes of evaporation and diffusion may be characterized by a scheme of energy levels involving the heat of adsorption of the unimolecular layer, the heat of liquefaction of water and the energies of activation corresponding to each of the two phases of the falling-rate period.

All species of non-fatty fish exhibit identical drying behaviour during both the constant-rate and the falling-rate periods.

Introduction

The annual world yield of fish and fish products is about 30 million tons[1] of which about half is marked fresh, frozen or canned, and about one-third is heavily salted, dried or smoked, or treated by a combination of these processes. The remainder, consisting of condemned and surplus fish and offal, is converted into fish-meal and fertilizer.

In certain processes, such as the smoke curing and salting of fish and the production of fish-meal and fertilizer, drying is an essential part of the process. Drying occurs, too, under certain conditions during cold storage, but such evaporative loss is undesirable.

Although most methods of fish preservation are traditional and often primitive, there is an impelling need to apply modern techniques, with the two-fold aim of increasing productivity and obtaining closer control of the process to achieve a uniform product. This requires that basic data on drying should be available together with a comprehensive knowledge of the fundamental principles involved. The present study was undertaken to obtain such data and to provide a basis for a detailed understanding of the process.

Investigations with materials other than fish have usually been based on studies of the effects of external conditions—such as temperature, humidity, air flow, etc.—and of the internal mechanism of liquid or vapour flow. It has now been well established that the initial rate of drying is determined by the external conditions.[2] The period during which these conditions are dominant, known as the constant-rate period, is terminated when the supply of water to the surface of the material is no longer capable of supporting this rate of drying. After this period, the rate of drying decreases continuously until finally it becomes vanishingly small. During this falling-rate period, the mechanism of internal flow dominates the rate of drying.

For fish muscle the constant-rate period appears to occupy a significant portion of the total drying time during most light curing processes, but where the flesh is almost completely dried the falling-rate period constitutes most of the drying time.

A few investigations of limited scope have been reported of the drying of heavily salted cod,[3] of caplin[4] and of herring,[5] but in each case these have been principally concerned with observations of drying behaviour during the falling-rate period. The present paper offers the results of a comprehensive examination of the behaviour of fish muscle, i.e., fillets, during both the constant-rate and the falling-rate periods. Theoretical explanations are advanced to describe the course of events during each of these periods and a theory is given which attempts to link the two sets of conditions, external and internal, so that a complete description of the whole drying process can be outlined.

Experimental

Material

The proteins of fish muscle consist of helical chains of amino-acids cross-linked in a gel system. The proteins are biologically organized inside cells which are jelly-filled sacs having

the form of thin fibres grouped together in a parallel array between thin sheets of connective tissue known as myocommata. While the myocommata traverse the thickness of the muscle, the cells are generally directed lengthwise, giving rise to a structural orientation in a system otherwise geometrically irregular.

The sagittal section of most species of 'round' fish is held in the vertical plane in the natural state. It is therefore convenient to refer the orientation of cut surfaces to the plane containing this section. A system of rectangular axes of co-ordinates Ox, Oy, Oz, with its origin at any arbitrary point O within the fish may be arranged so that the xy-plane lies parallel to the sagittal section. It follows then that the xy-plane corresponds to a vertical longitudinal section, the yz-plane to a transverse section and the zx-plane to a horizontal longitudinal section (Fig. 1).

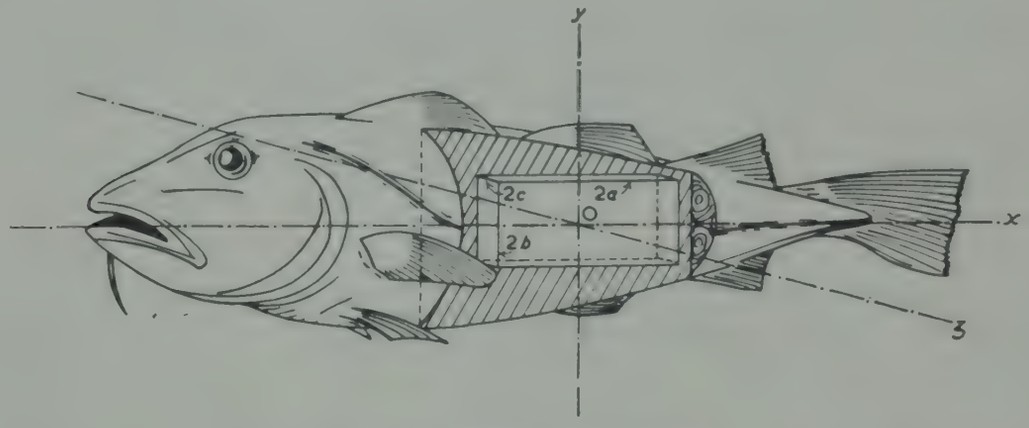

FIG. 1. *System of co-ordinates*

To facilitate subsequent calculations, pieces of fish fillets were cut in the form of rectangular parallelepipeds: owing to the limitations imposed by the shape of most fish, these fillet pieces were generally in the form of slabs cut parallel to the xy-plane. In certain indicated experiments slabs were cut parallel to the other principal planes. The dimensions of the fillet pieces $2a$, $2b$, $2c$ were therefore measured along the axes Ox, Oy, Oz respectively, as indicated in Fig. 1. In general, the side of length $2a$ was placed parallel to the direction of air flow.

Fillet pieces could not be cut with satisfactory precision unless the muscle was frozen, since in the unfrozen state the flesh was not sufficiently rigid.

The choice of species to be employed in these investigations was limited mainly to those fish from which large fillet pieces could be cut and in which the muscle contained only small traces of fat. Of these, the most readily available, cod (*Gadus callarias*), was most extensively used. Some data for cod muscle relevant to the problem of drying are given in Table I. The drying properties of some other species of fish were also examined, though in less detail, in order to compare the effects of the variation of tissue structure.

Normally, during drying, fillet pieces were placed on 8- or 12-mesh wire trays or $\frac{1}{2}$-in. expanded metal trays, the holes being sufficiently large to permit adequate ventilation of the lower surfaces of the fillet pieces.

Table I

Some properties of cod muscle

Density at 15°, undried	1·054 g./cm.^{3}
" " −1°, "	1·050 g./cm.^{3}
" " −5°, "	0·95 g./cm.^{3}
" " 15°, dry[6]	1·31 g./cm.^{3}
Water content[7]	80·3–82·6% of wet weight
Protein content[7]	15·0–19·0% of wet weight
Salt content (NaCl)	0·103–0·126% of wet weight
Fat content (including fat in lateral band)[7]	0·1–0·9% of wet weight

Apparatus

The work was carried out in an experimental recirculating wind tunnel of conventional design. The air velocity in the tunnel could be varied within the range 0 to 6 m./s. and the air temperature maintained within ±0·1°C of any desired value above room temperature up to 100°C. The velocity of the air stream was measured with a vane anemometer which had been

calibrated by the makers. The amplitude of temperature fluctuations was minimized by heating the tunnel with a 2kw-lamp for which the thermal time-constant was of the order of a few seconds. The lamp was operated through a relay controlled by a mercury-in-glass contact thermometer.

Relative humidity was maintained at any desired level above that permitted by the conditions of the ambient atmosphere using steam injected from a small electrically heated boiler. When the air velocity was in excess of about 3·5 m./s. control was sometimes effected by a second mercury-in-glass contact thermometer, arranged as a wet-bulb thermometer: the contacts operated a relay in the boiler heater circuit when the wet-bulb temperature fell below a preset value. This was achieved by sleeving the bulb with a linen wick, one end of which dipped into a constant-head container fed from a reservoir outside the wind tunnel (Fig. 2). In this way the wet-bulb temperature of the air could be maintained within $\pm 0{\cdot}25°$ without attention for a time which was limited only by the capacity of the reservoir.

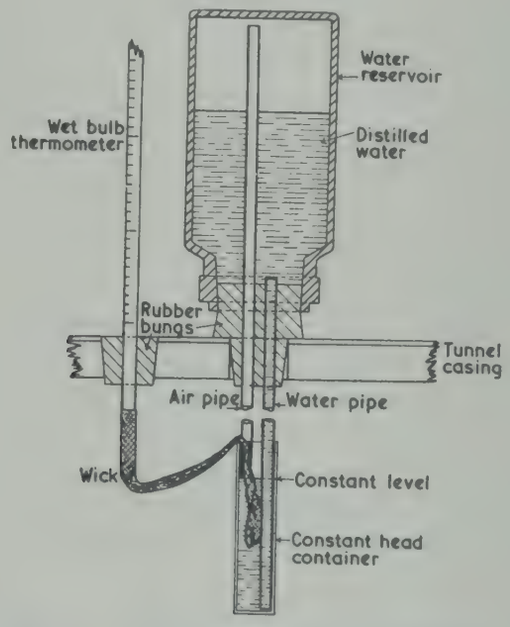

FIG. 2. *Method of feeding wet-bulb wick*

When the air velocity was less than the minimum necessary for accurate wet-bulb contro of relative humidity, i.e., about 2·5 m./s., the wet-bulb contact thermometer was replaced by a capacitance-resistance hygrometer element.[8] A current generated in the associated indicator operated control contacts which replaced the contacts of the wet-bulb thermometer but otherwise performed the same function. Using this means of control, relative humidity could be maintained within $\pm 0{\cdot}25\%$ at all air velocities.

Two frames containing a number of open-mesh wire trays were suspended horizontally in the air stream by means of rods which passed through holes in the top of the wind tunnel. The rods were attached to two indicating balances supported above the wind tunnel so that two independent sets of weighings could be obtained of the fish placed on the trays without removing the fish from the tunnel. One balance, capable of supporting a maximum load of 500 g. and having a chart range of 25 g., which could be read to an accuracy of $\pm 0{\cdot}05$ g., weighed small samples; the other, able to support 5 kg., range 500 g. and reading accuracy ± 1 g., weighed larger samples. At a later stage in the work, the 5-kg. balance was replaced by another 500-g. balance. In order to permit continuous weight indication as the samples dried, weights were automatically loaded on to the appropriate pan of each balance when the scale beams approached the stops. This was effected in each case by means of a claw wheel driven through a reduction gear by a small electric motor (Fig. 3). The motor was operated by an electronic relay triggered by a 'whisker' contact on the beam arm. Cylindrical mild steel weights of 20 g. and 400 g., for the light and heavy balances, respectively, were released from ramps as illustrated in Fig. 3. The rate of release was sufficiently slow to prevent a second weight from being loaded before it was required. The number of 20-g. weights released was recorded on a telephone subscribers' meter.

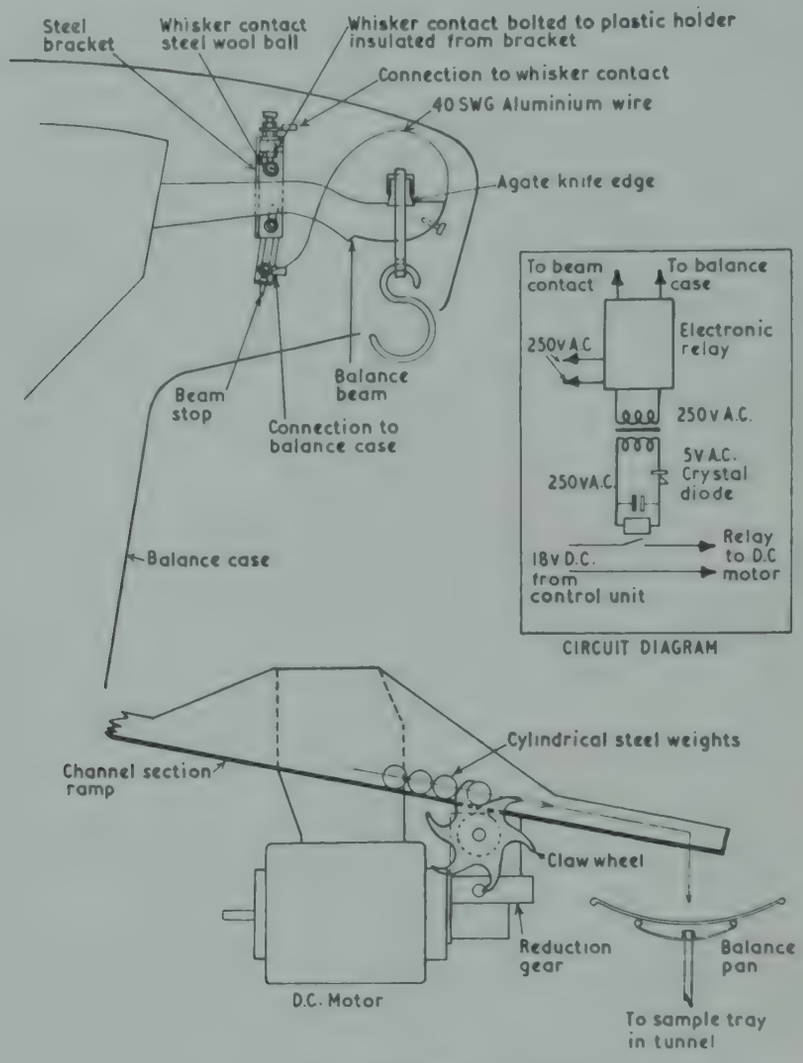

FIG. 3. *Weight-loading mechanism*

The balance charts were photographed periodically by an electrically operated single-shot 16 mm. camera. Special charts were prepared photographically for both balances so that each consisted of white figures and markings on a black background. The large balance was viewed by reflection in a mirror and, in order that readings could be made without effort, the chart facing the mirror was printed as a mirror image of the obverse scale. Also mounted in the field of view of the camera were the telephone subscribers' meter, a chronometer, and the indicating dials of mercury-in-steel wet- and dry-bulb thermometers placed in the tunnel. Fig. 4 shows the arrangement of the mechanism for bringing about the sequence of operations for obtaining the photographic record. A brief description will suffice to explain the functioning of this arrangement.

Contacts S1, operated by a self-resetting process-timing clock, initiate the sequence by charging a large condenser C1, shunted across the coil of a high-resistance magnetic relay MR1. One pair of contacts on this relay interrupts the switch contactor circuit of the fan motor, and a second pair of contacts operates the camera motor driving the film-winding and shutter-loading mechanism. The latter pair also operates an electro-pneumatic delay switch EPDS1, which switches a 100-w lamp for illuminating the balance charts. After the clock contacts have opened, relay MR1 remains energized (by the charge held by C1) for a period of time which is sufficiently long to allow the fan motor to stop and the balances to become steady. When the charge has leaked away sufficiently for relay MR1 to become de-energized, a third pair of contacts closes and condenser C3 is charged through the coil of relay MR2, which is thereby energized, and a pair of its contacts operate the camera shutter release solenoid. When MR1 is de-energized, the switch contactor circuit is once more energized and the fan motor resumes its operation. Shortly afterwards EPDS1 resets itself and extinguishes the lamp. The process-timing clock has by now reset itself and the control circuit is once more ready to repeat this sequence of operations.

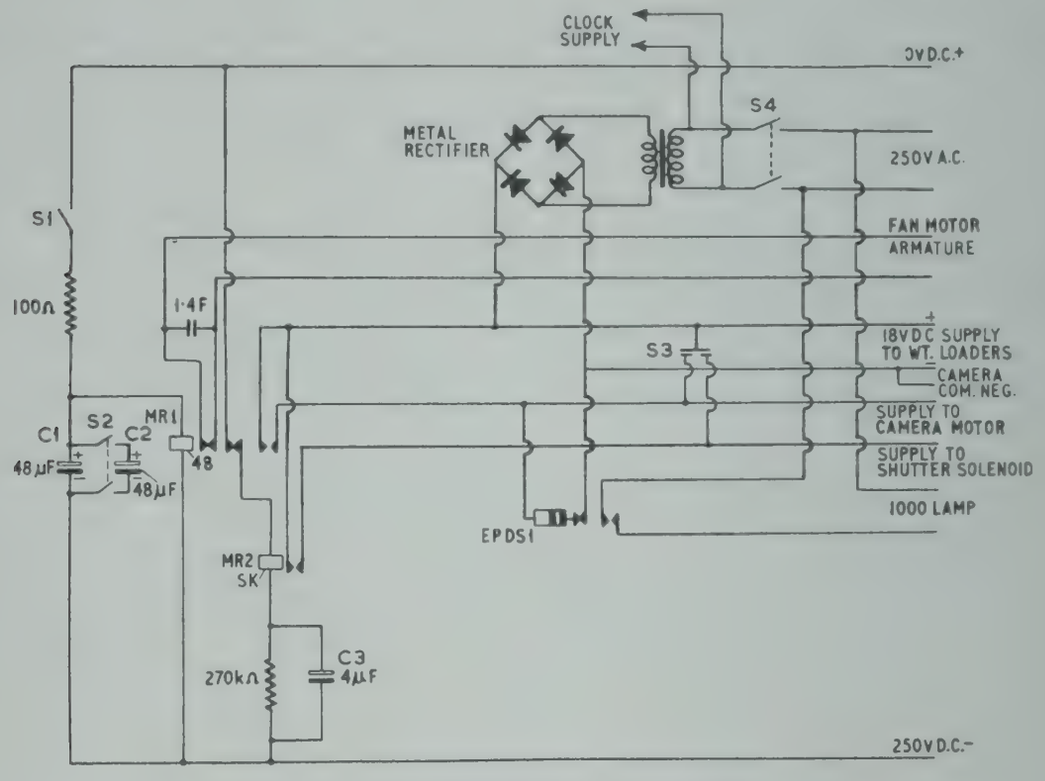

FIG. 4. *Circuit diagram of control unit*

S1 Clock contacts; S2 Operating switch for increased delay; S3 Push-button switch for manual operation of camera; S4 Main switch

The apparatus was capable of operating without attention for many days. For example, when hourly records were taken, this period extended to 40 days before the camera required reloading with film. An example of an enlarged photographic record is shown in Fig. 5. The apparatus has recorded approximately 75,000 weighings during a period of five years with very little supervision.

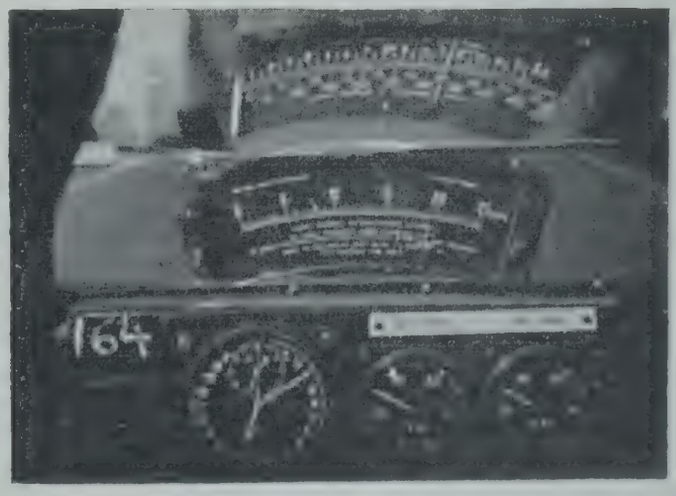

FIG. 5. *Photographic record enlarged from 16 mm. film*

Constant-rate period

General

It is usually assumed that the rate of drying of a solid substance during the constant-rate period corresponds to the rate of evaporation from a free-moisture surface on the solid and that when no free moisture remains, drying enters the falling-rate phase. The rate of evaporation of water from the surface during the constant-rate period is often expressed as a function of air velocity, wet-bulb depression, shape and area of the surface and direction of the air stream.

The purpose of the experiments described here was to discover the extent to which these considerations are applicable to fish muscle. At an early stage it was established that several fillet pieces, well separated on the drying trays, each behaved effectively as an individual piece; the data to be presented may therefore be regarded as applying to single fillet pieces drying in air under the conditions indicated, even though in some cases the number of pieces exceeded 400.

Fig. 6 illustrates a typical example of the initial drying behaviour of a cod fillet piece exposed to an air-stream in which the direction of flow was parallel to the longest edges. The curve showing the weight of the fillet piece W plotted against time, t, appears to be composed of at least two portions in each of which the gradient remains constant. Both periods are indicated as constant rates of drying in the curve showing the relationships between rate of drying dW/dt (obtained by numerical differentiation) and time. There is evidence of several other distinct, but shorter, periods during which the rate remains constant but becomes progressively smaller in each successive period. These features are typical of the initial drying behaviour of cod muscle observed in over 500 experiments and it is clear that such behaviour does not appear to be characterized by a *single* constant-rate period, as is commonly supposed for many other materials, but by several. The problem will be discussed in later sections in relation to measurements of the effective duration of the constant-rate period and to the theory of the constant-rate period, but at the moment it can be stated that there can be no *precisely* defined constant-rate period for a body of finite size.

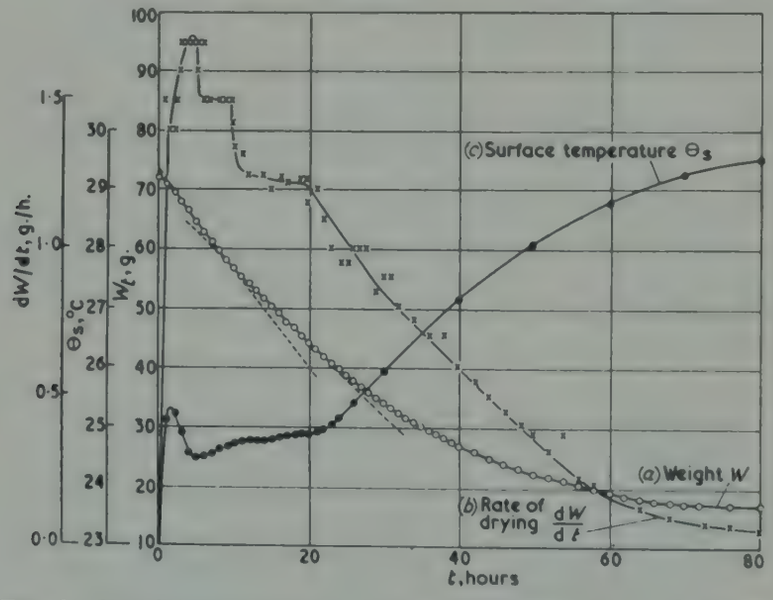

FIG. 6. *Initial drying behaviour of single fillet piece* 10 × 5 × 1·5 *cm. exposed to air stream of velocity* 30 *cm./sec. parallel to* 10-*cm. edges*

Dry-bulb temperature 30°; wet-bulb temperature 18°. Curve A: weight as a function of time; Curve B: rate of drying as a function of time; Curve C: temperature at centre of surface as a function of time

Mass- and heat-transfer

A volatile substance is transferred into a stream of air passing over its surface by diffusion through the layer of laminar flow adjacent to the surface and, mainly by turbulent mixing, into the zone beyond. The coefficient of mass-transfer, k_w, may be defined by the relation

$$-dW/dt = k_w A (p_s - p_a) \quad \ldots\ldots (1)$$

k_w being a function of the Reynolds number, W the weight of the substance, t time, A surface area, p_s the partial pressure of the vapour at the surface and p_a that of the vapour in the air. The substance loses heat, H, at a rate

$$-dH/dt = L(dW/dt) \quad \ldots\ldots (2)$$

where L, the latent heat of vaporization at a temperature θ_s, is given by Clapeyron's equation

$$dp_s/d\theta = L/T_s (v_2 - v_1) \quad \ldots\ldots (3)$$

v_1 and v_2 being the specific volumes of the substances in the solid or liquid phase and the vapour phase respectively, and $T_s = 273{\cdot}1 + \theta_s$. The surface temperature, θ_s, corresponds

to an equilibrium value at which the rate of heat gain by radiation and convection is equal to the rate of heat loss resulting from evaporative cooling. The rate of heat transfer is

$$dH/dt = k_h A (\theta_a - \theta_s) \quad \ldots\ldots (4)$$

k_h, is the effective heat transfer coefficient, being a function of the Reynolds number; θ_a is the air temperature. From equations (2) and (4) we have

$$-L(dW/dt) = k_h A (\theta_a - \theta_s) \quad \ldots\ldots (5)$$

The linear dependence of dW/dt on $\theta_a - \theta_s$ was verified directly for water evaporating from the surface of cod muscle by concurrently recording the surface temperature of one fillet piece and the weight of an identical piece placed alongside it in the air-stream. (The latter piece was that for which the data presented in Fig. 6 was obtained.) Temperature difference was measured by means of a thermocouple: one junction was inserted just beneath the upper surface at the centre of the fillet piece and the other junction was exposed to the air-stream. The conductors entering the fillet piece were threaded just beneath the surface and parallel to the leading edge in order to minimize errors resulting from heat conduction. The sides of length 2a of both fillet pieces were placed parallel to the direction of air flow. The curve showing the variation of surface temperature with time is superimposed on the rate curve in Fig. 6. From these two curves corresponding values of $\theta_a - \theta_s$ and dW/dt have been taken and plotted in Fig. 7. It can be seen that a linear relationship exists, as predicted by equation (5).

Combining equations (1) and (5) we have

$$\frac{p_s - p_a}{\theta_a - \theta_s} = \frac{1}{L} \cdot \frac{k_h}{k_w} \quad \ldots\ldots (6)$$

If the surface is saturated with the evaporating substance, p_s is related to θ_s by an expression of the form[4]

$$\log p_s = \alpha/T_s + \beta \log T_s - \gamma T_s + \delta T_s^2 - \zeta \quad \ldots\ldots (7)$$

where $T_s = 273{\cdot}1 + \theta_s$ and α, β, γ, δ, ζ are constants.

Now the ratio $k_h\, k_w$ is practically constant for convective heat- and mass-transfer except at low values of the Reynolds Number ($\lesssim 100$) below which the relative effect of natural evaporation becomes more pronounced. Under conditions of equilibrium and in the absence of heat transfer by radiation, $(p_s - p_a)/(\theta_s - \theta_a)$ is uniquely determined for given values of p_a and θ_a. θ_s is, in fact, identical with the wet-bulb temperature, θ_w, if the substance is water. Under these conditions equation (5) becomes

$$\frac{1}{A} \cdot \frac{dW}{dt} = -\frac{k_h}{L} (\theta_a - \theta_w) \quad \ldots\ldots (8)$$

and the rate of evaporation of water per unit area of a saturated surface is therefore proportional to the wet-bulb depression.

At low air velocity, the rate of heat transfer by convection is considerably reduced and becomes comparable with the rate of heat transfer by radiation. The effect is to diminish the value of $\theta_a - \theta_s$ below that of the wet-bulb depression, $\theta_a - \theta_w$, as the air velocity decreases. Finally, at zero air velocity, the temperature of the surface is determined by the effects of radiation and natural convection. An example of the effect of air velocity, v, on the temperature at the surface of cod muscle is given for a fillet piece 10 cm. × 5 cm. × 1·5 cm. in Fig. 8. $\theta_a - \theta_s$ was measured by means of thermocouples, one junction of which was inserted just beneath the upper surface at the point of intersection of the centre line with a line parallel to the leading edge at a distance of 1 cm., and the other junction was exposed to the air stream above the surface. It will be noted that, although the temperature of the surface initially falls steeply with increasing air velocity, it remains slightly higher than the wet-bulb temperature even at the highest velocity shown (366 cm./sec.); the probable causes of the difference being the practical difficulty of locating the point of the thermocouple sufficiently close to the surface, and the heating effects due to radiation.

Geometrical effects

The work to be described on the effects of the geometry of the system follows, where appropriate, the treatment given by Powell[10] to the problem of the evaporation of water from

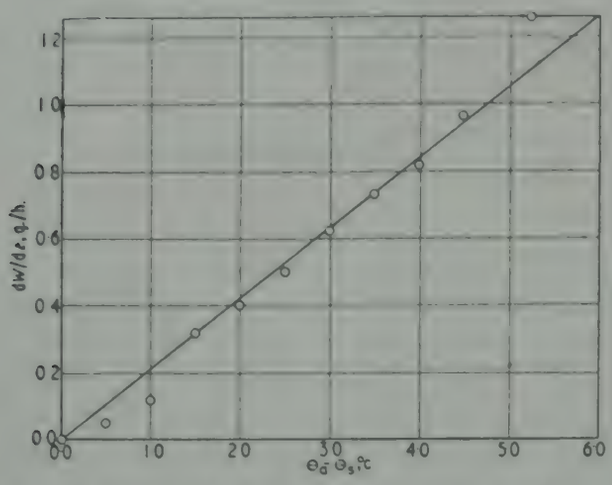

FIG. 7. *Relationship between surface cooling and rate of drying for fillet piece* 10 × 5 × 1·5 *cm. exposed to an air stream of velocity* 30 *cm./sec. parallel to* 10-*cm. edges*
Dry-bulb temperature 30°; wet-bulb temperature 18°

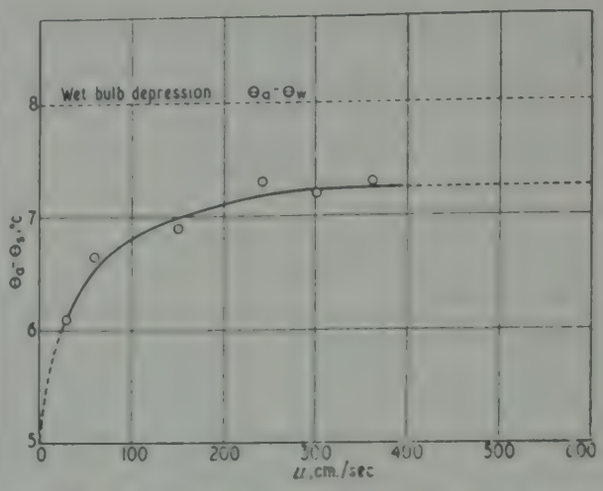

FIG. 8. *Effect of air velocity on temperature at surface of fillet piece* 10 × 5 × 1·5 cm.
Dry-bulb temperature 30°; wet-bulb temperature 22°

saturated surfaces. In the present work the system could not be idealized as for most saturated surfaces, owing to the limitations imposed by the nature of the material. It would have been difficult, for instance, to limit drying entirely to one face because the consequent slight shrinkage and distortion of the muscle would have impaired the effectiveness of masking of the other faces. In any case it was desirable to relate the experimental conditions as closely as possible to the conditions encountered in practice. These practical conditions could be simulated completely by studying the behaviour of whole fillets, but since these were of somewhat arbitrary shape, the results would not have been amenable to calculation. The fillet pieces were therefore always cut in the form of a rectangular parallelepiped which varied in shape from the largest cube to the longest and thinnest strip that could be cut from cod muscle.

The mean initial rate of evaporation per unit surface area was always taken to be that for the total surface, that is

$$\varepsilon = \frac{dW/dt}{8(ab + bc + ca)} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (9)$$

which follows from Powell's results. (These show that the extreme differences between the rates of evaporation from plane rectangular surfaces facing upstream and those facing downstream are not very considerable.) The values for the tangential position are intermediate between those for the two perpendicular positions when the product of air velocity and length of side parallel to the air stream is less than about 6000 cm.^{2} sec. The assumption implicit in equation (9), that the rate of evaporation is identical for all six surfaces, is therefore approximately correct for a cube. This is not true for samples of other shapes since the mean rate of evaporation per unit area varies with length of surface. The errors introduced by making the same assumptions will, however, be small for thin slabs because of the relatively small surface areas of the edges.

For a given set of conditions, the mean rate of drying per unit area, ε, varied considerably with the size of the smaller fillet pieces but was approximately independent of the total area of the larger fillet pieces. In order to compare data obtained under different conditions of humidity and temperature and to compare the results with those of Powell, the results were expressed as a mean rate of evaporation per unit area per unit vapour pressure difference, $\varepsilon/(p_s - p_a)$, i.e., the effective coefficient of mass-transfer. Values of $p_s - p_a$ were found by a method described later.

Experiments on the initial drying rates of cod fillet pieces of various lengths, l, measured parallel to the air stream were usually carried out with samples 0·5 cm. thick and 5 cm. wide. When l was 5 cm. or less the 'width' varied from 4 to 30 cm., it having been establishing that values of ε were not strongly dependent on this dimension in the range stated. The relationship between the mean rate of evaporation per unit area per unit vapour pressure difference and the length of fillet piece for various values of the air velocity, u, is shown in Fig. 9 together with the

curve (Fig. 12 of Powell's paper) for the rate of evaporation of water from a plane saturated surface of infinite width for an air velocity of 200 cm./sec. The results indicate that the rate of evaporation per unit area is substantially constant for fillet pieces longer than about 6 cm. at each velocity in the range investigated, and Powell's curve fits in well with the series of curves drawn through the experimental points, but for shorter lengths the form of the curves for fillet pieces does not correspond with that from streamlined saturated surfaces. As the length of the fillet piece is reduced, the rate of evaporation per unit area at each velocity increases to a maximum value at about 2 cm. and then diminishes as the length is reduced further. The reason for this behaviour is not understood but is probably associated with turbulence at the leading edge.

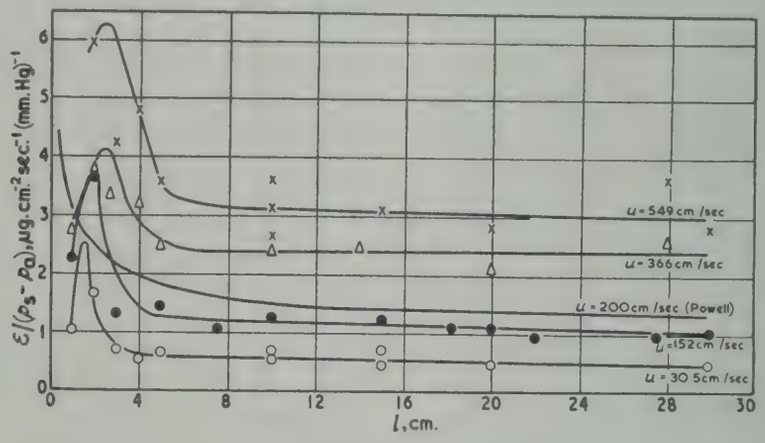

FIG. 9. *Rate of evaporation per unit area per unit vapour pressure difference plotted against length for various values of air-velocity*

Powell showed that by analogy with the problem of heat transfer by forced convection, all data for plane surfaces could be brought on to a single curve by plotting the rate of evaporation, due to unit vapour pressure differences, from a surface of unit width and length l, against the product of the air velocity and length of surface, i.e., $\varepsilon l/(p_s - p_a)$ against ul.

In order to evaluate the group $\varepsilon l/(p_s - p_a)$ in the present investigation it was necessary to obtain values of $p_s - p_a$ under each condition of air velocity and wet-bulb depression. The method was as follows. For a given air velocity the temperature at the surface was read from the curve drawn in Fig. 8. Assuming that there was free water at the surface, the vapour pressure was derived from tables,[9] and by subtracting from this the partial vapour pressure in the air stream, the vapour pressure difference for the given conditions was obtained. The further reasonable assumption was made that, as for a saturated surface, the vapour pressure difference between the surface and the air was proportional to the wet-bulb depression. It was then possible to construct a family of straight lines (Fig. 10) relating vapour pressure difference to the wet-bulb depression for the various values of air velocity at which the experiments were conducted.

With the aid of Fig. 10 all the data, for lengths ranging from 1 to 30 cm., air-velocities from 30 to 549 cm./sec. and values of wet-bulb depression from 1·4 to 14·8°, have been expressed as the rate of evaporation per unit width per unit vapour pressure difference, and these values of $\varepsilon l/(p_s - p_a)$ are plotted against the product of air velocity and length in Fig. 11.* The points lie about the mean curve for the evaporation of water from a plane saturated surface obtained by Powell (Fig. 16 of Powell's paper), given by the equation:

$$\varepsilon l/(p_s - p_a) = 2{\cdot}12 \times 10^{-7} l^{0{\cdot}77} (1 + 0{\cdot}121 u^{0{\cdot}85}) \quad \ldots\ldots (10)$$

where all the quantities are expressed in c.g.s. units. The agreement is sufficiently close to justify the conclusion that in the initial stages of drying the surface of cod muscle behaves as though it were saturated with water and the rate of evaporation is identical with that of free water.

*In Fig. 11 (and in succeeding figures) in which the number of determinations exceeds 4, the mean value and standard deviation are indicated by a point and a vertical line: a numeral close to the point gives the number of determinations.

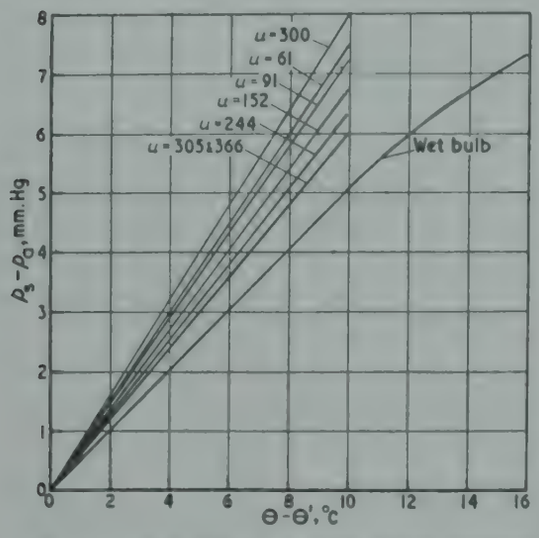

FIG. 10. *Relationship between vapour pressure difference at surface of a fillet piece and wet-bulb depression at* $\theta_a = 30°$ *for various velocities of incident air stream*
(*u* in cm./sec.)

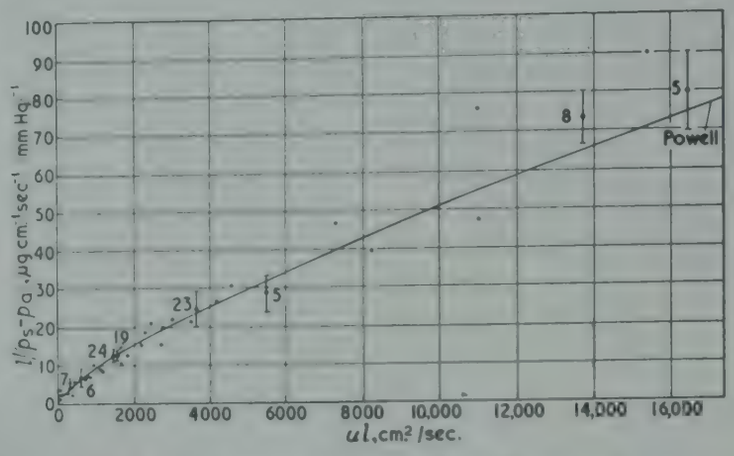

FIG. 11. *Rate of evaporation per unit width per unit vapour pressure difference from surface of fillet piece* 1 *cm. long as a function of the product* ul
Vertical lines indicate standard deviations; numerals indicate number of determinations

Duration of constant-rate period

It was observed earlier that no *single* constant-rate period characterizes the initial drying behaviour of cod muscle, but an attempt will now be made to show that there exists an effective constant-rate period and that its duration can be defined and determined with reasonable accuracy.

It appears from the above results that the local rate of evaporation per unit area decreases with the distance from the leading edge of a fillet piece. An indication of the magnitude of the effect may be obtained assuming equation (10) to hold for evaporation from the four surfaces tangential to the air stream. If, then, ε_x denotes the local rate of evaporation per unit area at a distance x from the leading edge, we may rewrite equation (10) as follows

$$\int_0^x \varepsilon_x \, dx = 2{\cdot}212 \times 10^{-7} x^{0{\cdot}77} (1 + 0{\cdot}121 u^{0{\cdot}85}) (p_s - p_a) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (11)$$

and by differentiation obtain

$$\varepsilon_x = 1{\cdot}70 \times 10^{-7} x^{-0{\cdot}23} (1 + 0{\cdot}121 u^{0{\cdot}85}) (p_s - p_a) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (12)$$

For a fillet piece of total length l the local rate of evaporation expressed as a fraction of the mean rate over the whole area is:

$$\varepsilon_x/\varepsilon = 0{\cdot}77(x/l)^{-0{\cdot}23} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (13)$$

Values of $\varepsilon_x/\varepsilon$ for various values of x/l are tabulated below:

x/l	$\varepsilon_x/\varepsilon$	x/l	$\varepsilon_x/\varepsilon$	x/l	$\varepsilon_x/\varepsilon$
0 ..	.. ∞	0·3 ..	.. 1·014	0·7 ..	.. 0·836
0·05	.. 1·887	0·4 ..	.. 0·948	0·8 ..	.. 0·810
0·1 ..	.. 1·307	0·5 ..	.. 0·902	0·9 ..	.. 0·785
0·2 ..	.. 1·111	0·6 ..	.. 0·866	1·0 ..	.. 0·770

At the leading edges the local rate of evaporation is infinite but falls rapidly to a value corresponding to the mean rate for the whole fillet at slightly less than one-third of the distance along its length. The local rate at the centre is 90% of the mean rate for the whole fillet. Equation (10) shows that, within about 1%, this represents the mean rate for all except the first fifth of its length. Under practical conditions, the additional turbulence introduced by the sharp leading edges of a fillet piece leads to a less pronounced variation of ε_x with x than is suggested by equation (13) and the effect is to smooth out the peak at the leading edge, as is demonstrated in Fig. 9. It is convenient therefore to divide each of the four surfaces tangential to the air stream into two arbitrary zones: (1) $0 < x/l < 0{\cdot}2$ in which the mean rate of evaporation

is considerably greater than from the remainder of the surface; and (2) $0{\cdot}2<x/l<1$ in which the mean rate of evaporation may be represented by the local rate at $x/l = 0{\cdot}5$ and in which the local rate elsewhere in this zone may be regarded as being constant.

Initially, the total rate of evaporation from the fillet piece (neglecting the end surfaces) is composed of the contributions from both these zones and the rate is constant for a short while, but owing to the relatively rapid rate of evaporation in zone 1, the amount of water available at the surface soon becomes inadequate to maintain the supply and the rate rapidly declines to a value controlled by liquid diffusion within the fillet piece. The principal contribution then comes from zone 2 and the rate remains substantially constant for a further period of time until here, too, the rate of supply of water becomes inadequate. The resultant effect is therefore an initial ' constant-rate ' period while zone 1 is contributing, followed by a second constant-rate period when the contribution from zone 1 becomes negligible. The actual behaviour is certainly more complicated than this and probably follows the pattern shown schematically in Fig. 12, but the main features of this behaviour as exemplified in Fig. 6 conform to the crude analysis. Further support for the assumption that the mean rate of drying in zone 2 may be represented by the local rate at the centre of each surface is derived from the rapid rise in surface temperature at this point which accompanies the end of the final period of constant rate.

On the basis of the foregoing, the duration of the effective constant-rate period is defined as the period during which the rate of evaporation from the centre of the surface remains constant, and is denoted by the symbol t_c. It is assumed that the local rate of evaporation remains constant at each point along the length of the fillet piece from the commencement of drying until the local rate of supply of water at the centre of the fillet piece becomes inadequate, so that t_c also represents the time at which the constant-rate conditions effectively terminate.

In practice, t_c is usually indicated in the drying curve by a change of slope at the lower end of the last (and usually the longest) straight portion. The accuracy in estimating this point is of the order of $t_c/20$. It may be seen in Figs. 6 and 7 that the termination of the effective constant-rate period is followed by a sharp rise of surface temperature.

In consequence of the variation with distance downstream of the local rate of evaporation, the duration of the effective constant-rate period varies with the length of the fillet piece as shown in Fig. 13. For each value of air velocity in the range 30 to 549 cm./sec., t_c initially increases with l and then appears to become constant as l increases further. Although the value of l at which t_c becomes constant is somewhat uncertain owing to the scatter of the points, it may roughly be estimated that this value is about 4 or 5 cm. for the highest air velocity and about 10 cm. for the lowest air velocity.

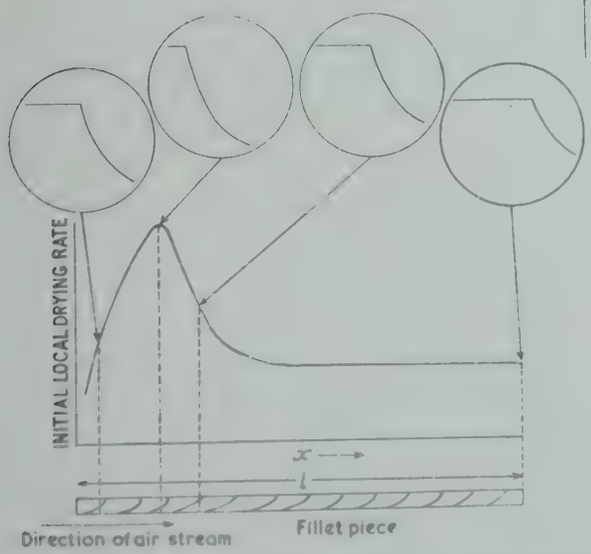

FIG. 12. *Schematic representation of local drying behaviour along length of fillet piece*
Inset diagrams represent rate curves at points indicated.

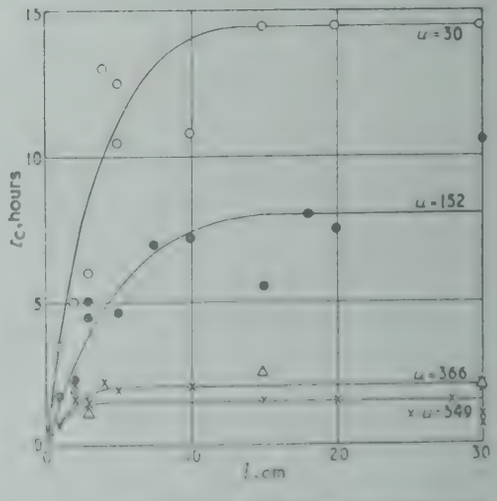

FIG. 13. *Duration of effective constant-rate period for various lengths of fillet piece*
0·5 *cm. thick at* $\theta_a = 30°$
Wet-bulb depression 8·0°; u in cm./sec.

Other factors which affect the duration of the effective constant-rate period are air velocity, wet-bulb depression, dry-bulb temperature, initial moisture concentration and thickness of fillet piece. The effects of air velocity and wet-bulb depression are shown in Figs. 14 and 15 respectively for fillets pieces of length 10 cm.

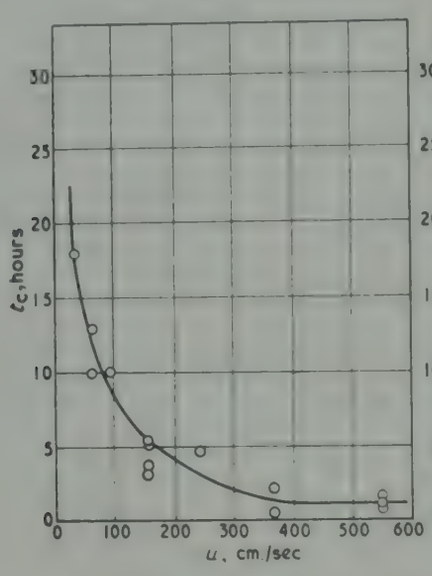

FIG. 14. *Effect of air velocity on duration of effective constant-rate period for fillet pieces* 0·5 *cm. thick and* 10 *cm. long*
Dry-bulb temperature 30°
Wet-bulb temperature 18°

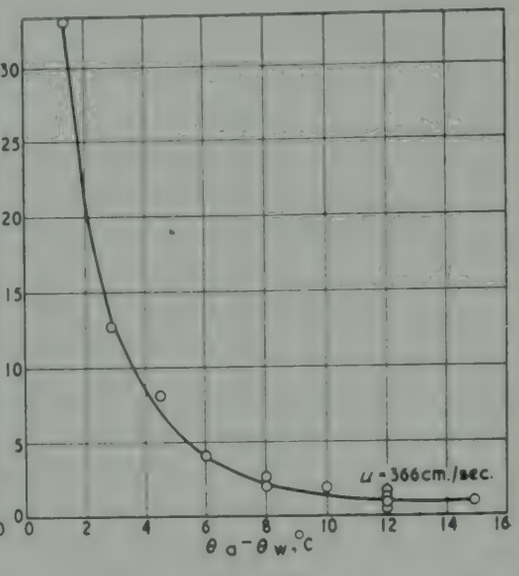

FIG. 15. *Effect of wet-bulb depression on duration of effective constant-rate period for fillet pieces* 10 × 5 × 1·5 *cm. exposed to air stream of velocity* 366 *cm./sec.*

In the discussion the constant-rate period will be considered in relation to the diffusion of water within the sample and a mathematical treatment unifying the effects of evaporation and diffusion processes will be advanced.

Effect of air condition on rate of drying

Under conditions of constant temperature and air velocity, the rate of evaporation per unit area as expressed in equation (1) may be modified by the assumption, previously made, that the vapour-pressure difference is proportional to the wet-bulb depression, thus:

$$-(dW/dt)/A = \varepsilon = \text{constant} \times k_w(\theta_a - \theta_w) \quad \ldots\ldots (14)$$

k_w is a function of D_a, the coefficient of diffusion of water vapour in air,[11] and therefore depends on temperature, but since D_a varies only slightly with temperature (at 20° D_a = 0·249 cm.²/sec. and at 40° D_a = 0·279 cm.²/sec.),[12] the rate of drying will be proportional to the wet-bulb depression at all temperatures within the range studied. In Fig. 16 the relationship between the initial rate of drying per unit area and wet-bulb depression is shown for cod fillet pieces 10 × 5 × 1·5 cm. exposed to an air stream of velocity 366 cm./sec. The results obtained at each of the temperatures indicated may be represented by a common straight line as expected.

In Fig. 17 the logarithm of the rate of evaporation per unit area per unit wet-bulb depression for cod fillet pieces of length 10 cm. or more is plotted against the logarithm of the air velocity. The points are scattered about a straight line which may be represented by the equation

$$\varepsilon/(\theta_a - \theta_w) = 1{\cdot}65 \times 10^{-8}\, u^{0{\cdot}77} \quad \ldots\ldots (15)$$

where all the quantities are in c.g.s. units. The numerical constant may be compared with the value of the convection heat-transfer coefficient $h_c = 3{\cdot}42 \times 10^{-8}$ in the heat-transfer expression

$$\varepsilon/(\theta_a - \theta_w) = 3{\cdot}42 \times 10^{-8}\, u^{0{\cdot}8} \quad \ldots\ldots (16)$$

recommended[2] for the constant rate in drying from plane saturated surfaces. The difference may be attributed in part to the fact that the surface temperature of the fillet pieces was always greater than the wet-bulb temperature (cf. Fig. 7). No significance is attached to the difference in the power to which the velocity is raised, as the accepted value of 0·8 is within the limits of experimental error in the present determination.

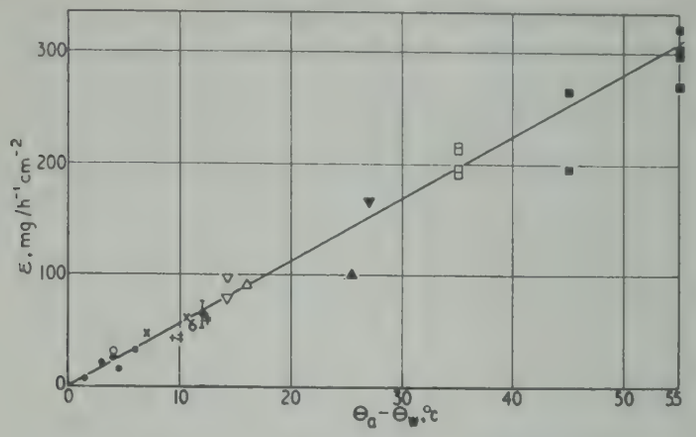

FIG. 16. *Effect of wet-bulb depression on rate of drying per unit area of fillet pieces exposed to air stream of velocity 366 cm./sec. at various dry-bulb temperatures*

○ 20°; × 25°; ● 30°; + 40°; △ 50°; ▽ 60°; ▲ 70; ▼ 80°; □ 90°; ■ 100°

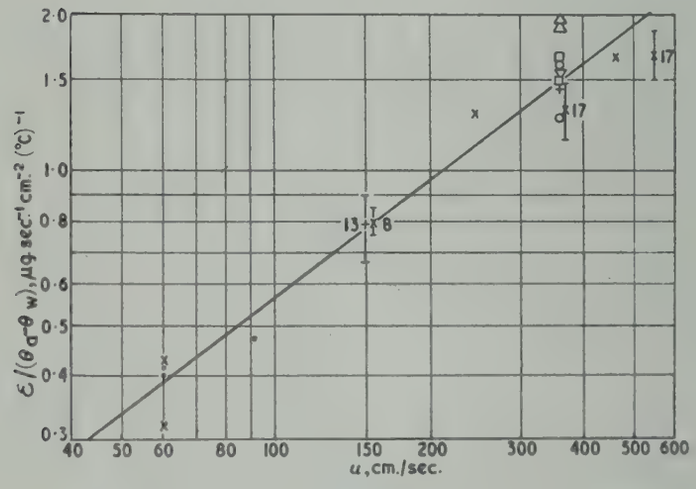

FIG. 17. *Relationship between logarithm of rate of evaporation per unit area per unit wet-bulb depression and logarithm of air velocity for fillet pieces of length 10 cm. or more*

θ_a—θ_w: ▽ 1·4°C; △ 2·9°C; □ 6·0°C; + 8·0C; ○ 10·0C; × 12·0°C; ● 14·8°C

Although equation (15) does not take into account the effect of length, as does equation (10), it offers a more direct method of calculating the initial rate of evaporation from the surface of fish fillets for a given set of conditions.

Falling rate period

General

The termination of the constant-rate period is followed by a rapid decline in the drying rate (see Fig. 6). The rate of drying continues to decrease and becomes negligibly small as the moisture content of the fish muscle approaches an equilibrium value. During the falling-rate period the drying behaviour of fish muscle under all conditions investigated follows a common pattern if the results are suitably presented. In Fig. 18, which is typical, the difference between the equilibrium weight, W_e, and the weight, W_t, at time t after the commencement of drying is plotted on a logarithmic scale as a function of time. Over the greater part of the curve the results may be represented by two straight lines, LL and MM, intersecting at a point O. The equations of these lines are

$$\ln (W_t - W_e) = \ln (W_t - W_e)' - t/\tau_i \quad \ldots\ldots (17)$$

$$\text{and } \ln (W_t - W_e) = \ln (W_t - W_e)'' - t/\tau_{ii} \quad \ldots\ldots (18)$$

where $\ln (W_t - W_e)'$ and $\ln (W_t - W_e)''$ are intercepts on the ordinate and τ_i and τ_{ii} are

constants. τ_i and τ_{ii} have the dimensions of time and both characterize the drying behaviour during each phase of the falling-rate period. By analogy with the discharge of condensers these are termed ' drying time-constants '.

The amount of water available during drying (the free water) is dependent on the equilibrium water content corresponding to the given conditions of relative humidity and temperature of the air. The relationship between equilibrium water content and relative humidity, determined by the method described by Gane,[13] is shown for cod muscle in Fig. 19. The water content was determined by oven-drying the samples at 102° for 24 hours. Provided the same procedure is used each time, reproducibility of the results is good.[14]

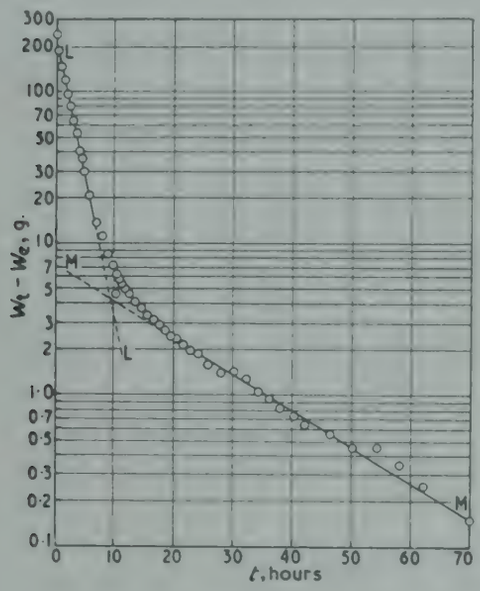

FIG. 18

FIG. 18. *Amount of free water remaining in fillet piece* 10 × 5 × 0·60 *cm. as function of time*
Dry-bulb temperature 35°; wet-bulb temperature 20·3°; air velocity 366 cm./sec.

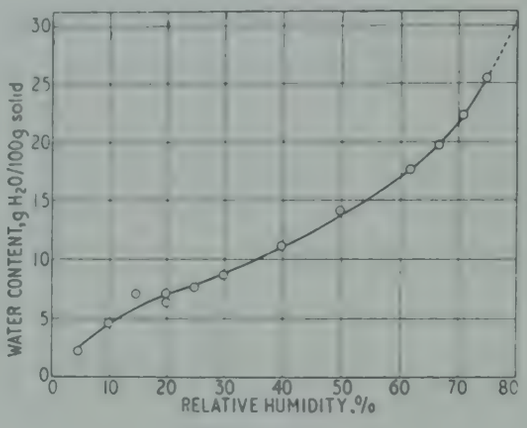

FIG. 19

FIG. 19. *Relationship between equilibrium water content of 2·5-cm. cubes of cod muscle and relative humidity at* 30°

In practice it was a simple matter to determine the equilibrium weight of a sample by inspection of the drying curve and thus to obtain the amount of free water at any time during drying. In plotting the logarithm of the free water against time, the slope of the first straight portion of the curve, LO, could be determined with an accuracy of about 1%. An indication of the satisfactory reproducibility of the method is given in Table II which shows pairs of values of τ_i determined in several experiments in which two groups of cod fillet pieces of identical shape were dried simultaneously.

Table II

Simultaneously determined values of drying time-constant τ_i *for two groups of cod fillet pieces of identical shape*

Size of pieces 10 × 5 × 1·5 cm. nominal thickness.
Air temperature 30°C.

Run No.	No. of samples in group	Mean thickness, cm.	τ_i, h.
30 A	6	1·35	16·6
30 B	6	1·36	16·6
31 A	6	1·40	14·3
31 B	6	1·42	14·3
38 A	6	1·52	15·2
38 B	3	1·76	17·6
79 A	2	1·50	14·0
79 B	2	1·52	14·4
80 A	8	1·58	17·6
80 B	1	1·62	18·5
83 A	9	1·42	17·1
83 B	5	1·47	17·1

Each pair of results is seen to agree closely and such differences as are observed probably arise from small variations in the mean thickness of each group of fillet pieces.

The results of 53 determinations of τ_i for fillet pieces 10 × 5 cm. of nominal thickness 1·5 cm. are represented in the form of a histogram in Fig. 20 (p.120). Values of τ_i have been corrected for small variations of thickness as described below. A Gaussian curve superimposed on the histogram shows that the distribution in values of τ_i is approximately normal and that for the size of fillet piece studied the mean time constant is 16·71 h., with a standard deviation of ±1·87 h. The standard deviation is somewhat larger than the differences observed in Table II and this can only be ascribed to biological variations such as changes in the structure and composition of the muscle accompanying seasonal fluctuations, and variation in the size of fish. No attempt was made to investigate these factors. It is assumed that a standard deviation of about ±11% represents the dispersion in the value of τ_i due to all causes.

The existence of the second part of the falling-rate period characterized by τ_{ii} was not normally apparent except when drying was continued for much longer periods than τ_i. Even when the time was considerably protracted, the loss of weight during this second part of the period was invariably so small that τ_{ii} could be determined only approximately. In the present paper the term ' drying time-constant ' will apply to the first part of the falling-rate period unless otherwise stated.

Without attempting to give an account of the basic mechanism giving rise to the observed behaviour during the falling-rate period, it will be assumed that Fick's Law is applicable to the movement of water in fish muscle, i.e., the flux, f, at a point at which the concentration of water is C is given by the expression

$$f = -D_e \text{grad } C \quad \ldots\ldots (19)$$

D_e being the effective diffusion coefficient. The rate of gain of water in an elemental volume dv is

$$dv.\frac{\partial C}{\partial t} = -dv \text{ div } f \quad \ldots\ldots (20)$$

$$\therefore \frac{\partial C}{\partial t} = \text{div } (D_e \text{grad } C) \quad \ldots\ldots (21)$$

In the case of an isotropic medium

$$\frac{\partial C}{\partial t} = D_e \nabla^2 C \quad \ldots\ldots (22)$$

If D_x, D_y, D_z represent the diffusion coefficients along rectangular axes x, y, z respectively, then

$$\frac{\partial C}{\partial t} = D_x \frac{\partial^2 C}{\partial x^2} + D_y \frac{\partial^2 C}{\partial y^2} + D_z \frac{\partial^2 C}{\partial z^2} \quad \ldots\ldots (23)$$

The solution of equation (23) follows that given by Carslaw & Jaeger[15] for anisotropic heat conduction.

In the region

$$-a<x<a,\ -b<y<b,\ -c<z<c$$

where the boundary conditions for the solution of this equation are

(i) $C = C_o$ when $t = 0$.

(ii) $C = C_e$ at $x = -a, a;\ y = -b, b;\ z = -c, c$ when $t>0$.

$$C = C_e + \frac{64}{\pi^3}(C_o - C_e) \sum_{l=0}^{\infty}\sum_{m=0}^{\infty}\sum_{n=0}^{\infty} \frac{(-1)^{l+m+n}}{(2l+1)(2m+1)(2n+1)} \times \cos\frac{(2l+1)\pi x}{2a} \cdot \cos\frac{(2m+1)\pi y}{2b} \cdot \cos\frac{(2n+1)\pi z}{2c} \exp(-t\alpha_{l,m,n}) \quad \ldots\ldots (24)$$

where $\alpha_{l,m,n} = \frac{\pi^2}{4}\left[D_x\frac{(2l+1)^2}{a^2} + D_y\frac{(2m+1)^2}{b^2} + D_z\frac{(2n+1)^2}{c^2}\right]$ ..... (25)

l, m, n being integers.

The average free water concentration is

$$\overline{C - C_e} = \frac{8(C_o - C_e)}{\pi^3 abc} \int_{-a}^{a}\int_{-b}^{b}\int_{-c}^{c} \sum_{l=0}^{\infty}\sum_{m=0}^{\infty}\sum_{n=0}^{\infty} \frac{(-1)^{l+m+n}}{(2l+1)(2m+1)(2n+1)} \times$$

$$\cos\frac{(2l+1)\pi x}{2a} \cdot \cos\frac{(2m+1)\pi y}{2b} \cdot \cos\frac{(2n+1)\pi z}{2c} \exp(-t\alpha_{l,m,n})dx\,dy\,dz \quad \ldots\ldots (26)$$

$$\text{Thus} \quad \frac{\overline{C - C_e}}{C_0 - C_e} = \left(\frac{8}{\pi^2}\right) \frac{\exp(-t \cdot \alpha_{lmn})}{(2l+1)^2(2m+1)^2(2n+1)^2} \quad \ldots\ldots (27)$$

$$= \left(\frac{8}{\pi^2}\right) \exp\left[-\frac{\pi^2}{4}\left(\frac{D_x}{a^2} + \frac{D_y}{b^2} + \frac{D_z}{c^2}\right) t\right] + \frac{1}{9}\exp\left[-\frac{\pi^2}{4}\left(\frac{9D_x}{a^2} + \frac{D_y}{b^2} + \frac{D_z}{c^2}\right)t\right] +$$

$$\exp\left[-\frac{\pi^2}{4}\left(\frac{D_x}{a^2} + \frac{9D_y}{b^2} + \frac{D_z}{c^2}\right) t\right] + \exp\left[-\frac{\pi^2}{4}\left(\frac{D_x}{a^2} + \frac{D_y}{b^2} + \frac{9D_z}{c^2}\right)t\right] \quad \ldots\ldots (28)$$

For values of $t \gtrsim 1/\alpha_{l,m,n}$ the series converges rapidly so that

$$\frac{\overline{C - C_e}}{C_0 - C_e} \simeq \left(\frac{8}{\pi^2}\right)\exp\left[-\frac{\pi^2}{4}\left(\frac{D_x}{a^2} + \frac{D_y}{b^2} + \frac{D_z}{c^2}\right) t\right] \quad \ldots\ldots (29)$$

Now $W_t - W_e = 8abc\,\overline{(C - C_e)}$

and $W_o - W_e = 8abc\,\overline{(C_o - C_e)}$

so that equation (29) becomes

$$\frac{W_t - W_e}{W_o - W_e} \simeq \left(\frac{8}{\pi^2}\right) \exp\left[-\frac{\pi^2}{4}\left(\frac{D_x}{a^2} + \frac{D_y}{b^2} + \frac{D_z}{c^2}\right) t\right] \quad \ldots\ldots (30)$$

Thus if the logarithm of the weight of free water in a sample of dimensions $2a$, $2b$, $2c$ is plotted against time, the curve will ultimately become a straight line of slope

$$S = -\frac{\pi^2}{4}\left(\frac{D_x}{a^2} + \frac{D_y}{b^2} + \frac{D_z}{c^2}\right) \quad \ldots\ldots (31)$$

This behaviour has already been demonstrated experimentally.

If the medium is isotropic, i.e., $D_x = D_y = D_z = D_e$, and D_e is assigned values D_i and D_{ii} in the first and second phases respectively of the falling-rate period, then S corresponds to $1/\tau_i$ in equation (17) and to $1/\tau_{ii}$ in equation (18). Thus,

$$D_i = 4/\pi^2\tau_i\,(a^{-2} + b^{-2} + c^{-2}) \quad \ldots\ldots (32a)$$

$$\text{and } D_{ii} = 4/\pi^2\tau_{ii}\,(a^{-2} + b^{-2} + c^{-2}) \quad \ldots\ldots (32b)$$

If D_e can be regarded as constant, then both τ_i and τ_{ii} should be proportional to the shape factor

$$F = (a^{-2} + b^{-2} + c^{-2})^{-1} \quad \ldots\ldots (33)$$

$(a^{-2} + b^{-2} + c^{-2})^{-\frac{1}{2}}$ is half the effective thickness of the slab, which reduces to c when $a = b = \infty$ in the case of an infinite slab.

Effect of shape

Drying time-constants were determined from the drying curves of cod fillet pieces cut in a wide variety of shapes and sizes varying from slices 2 mm. thick to slabs 20 cm. long and cubes with 4-cm. edges. Details of these experiments are given in Table III. All the results relate to determinations made at 30°.

Equation (32) is valid provided the following conditions are satisfied:

(i) the medium is isotropic.

Table III

Drying time-constants for cod fillet pieces of various dimensions at 30°C

Run No.	θ_w, °C	a, cm.	b, cm.	c, cm.	τ_i, h.
—	—	5·0	2·5	0·750	16·71 ± 1·87*
—	—	5·0	2·5	0·250	2·33 ± 0·46†
16A	15·2[a]	10·0	5·0	0·800	20·6
18A	14·2[b]	5·0	2·5	0·650	14·9
20A	15·2	5·0	2·5	0·940	25·3
22A	15·2	5·0	2·5	0·657	12·6
23A	15·2	5·0	2·5	0·380	4·88
24A	15·2	1·94	1·94	1·94	37·8
25A	15·2	0·50	0·50	0·50	2·37
26A	15·2	0·50	0·50	0·50	3·03
26B	15·2	5·0	2·5	0·313	4·12
27A	15·2	1·25	1·25	1·25	15·3
51A	12·0	0·25	0·25	0·250	0·84
72B	12·0	0·50	0·50	0·500	2·93
75A	12·0	10·0	5·0	0·134	0·80
75B	12·0	10·0	5·0	0·110	0·60
76A	12·0	5·0	2·5	0·370	5·29
77A	12·0	10·0	5·0	0·490	8·46
77B	12·0	10·0	5·0	0·313	3·60
86B	12·0	5·0	2·5	0·190	1·86
87B	12·0	5·0	2·5	0·158	1·00
91B	12·0	12·5	5·0	0·550	10·15
92B	12·0	0·085	2·0	2·0	0·243
93B	12·0	2·0	0·085	2·0	0·295
94B	12·0	2·0	2·0	0·099	0·326
98B	12·0	0·255	2·0	2·0	2·82
99B	12·0	2·0	0·273	2·0	2·70
100B	12·0	2·0	2·0	0·295	2·70
101B	12·0	0·233	2·0	2·0	2·13
102B	12·0	2·0	0·255	2·0	2·10
103B	12·0	2·0	2·0	0·285	2·25
104B	12·0	0·245	2·0	2·0	1·95
105B	12·0	2·0	0·248	2·0	1·78
106B	12·0	2·0	2·0	0·282	2·39
108B	12·0	0·512	0·512	0·512	3·00
109B	12·0	1·03	1·03	1·03	13·8
110B	12·0	1·57	1·57	1·57	23·7
111B	12·0	2·06	2·06	2·06	37·8
114B	12·0	2·0	2·0	0·283	2·23
159B	8·0	p·251	2·0	2·0	2·76
160B	8·0	2·0	0·264	2·0	2·54
162B	8·0	1·97	1·97	1·97	39·9
163B	8·0	2·0	2·0	0·255	2·39
164B	8·0	2·0	0·258	2·0	2·00
161B	8·0	2·03	2·03	2·03	35·4
165B	8·0	0·283	2·0	2·0	3·43
166B	8·0	2·0	0·276	2·0	2·97
167B	8·0	2·0	2·0	0·273	2·56
168B	12·0	2·5	2·5	0·305	3·47
169B	12·0	2·5	2·5	0·296	3·47
170B	12·0	2·5	2·5	0·279	2·82
171B	12·0	2·5	2·5	0·276	2·82
181A	8·0[c]	13·75	5·25	0·960	27·1
186A	8·0[c]	9·1	3·85	1·25	40·4
187A	8·0[c]	11·5	4·9	0·880	27·8

*Mean of 53 determinations. †Mean of 10 determinations.
a All air velocities 366 cm./sec. unless otherwise indicated. b Air velocity = 610 cm./sec.
c Air velocity = 152 cm./sec.
Brackets indicate that fillet pieces were all cut from same fish.

(ii) D_e is independent of c, (iii) of t and, (iv) of shrinkage.

In Fig. 21 values of the drying time-constant, τ_i, obtained from Table IV are plotted against the shape factor $(a^{-2} + b^{-2} + c^{-2})^{-1}$ on logarithmic scales. The best straight line through these points, obtained by the method of least squares, is expressed by the equation

$$\tau_i = 30{\cdot}1\ (a^{-2} + b^{-2} + c^{-2})^{-0{\cdot}923}$$

It will be observed that the index differs slightly from the value of unity suggested by equation (33). Such a difference could result from the preponderance of results for thin sections cut parallel to the xy-plane if the medium were anisotropic to the diffusion of water, but it will be

shown later that directional effects are small and lead to a value of the index which would slightly *exceed* unity. The most probable explanation for the observed difference is that it may be attributed to a reduction in the effective diffusion constant in the thinner samples, consequent on the greater relative effect of evaporative cooling. This follows from equations (2) and (30) which show that the rate of cooling per unit weight of free water is given by

$$\frac{dH/dt}{W_t - W_e} = \frac{L\,\pi^2 D_z}{4c^2} \qquad (34)$$

Hence, the effect of cooling varies inversely with the square of the thickness of the fillet and directly with the effective diffusion constant. Now, as will be shown later, D_z decreases with decreasing temperature, and the net effect for a given set of conditions is that the value of D_z in a thin sample will be less than that in a thick sample. Therefore values of τ_i will be relatively high for thin samples, and hence for low values of $(a^{-2} + b^{-2} + c^{-2})^{-1}$ and will tend to skew the line drawn through the points in Fig. 21 to a slightly smaller slope than is predicted by theory for an isotropic medium. It is very probable, therefore, that if the results are suitably corrected for the effects of cooling, the slope will be even closer to the theoretical value than the results indicate.

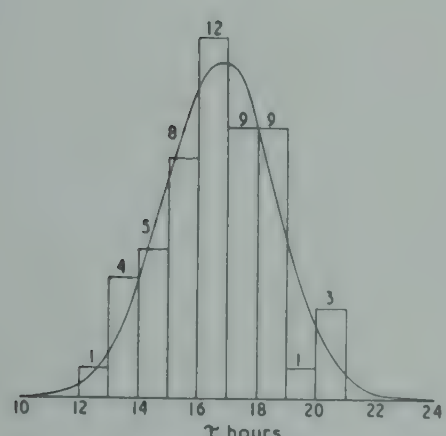

FIG. 20. *Frequency distribution of drying time-constants, τ_i, at* 30° (53 cod fillet pieces 10 × 5 × 1·5 cm.)

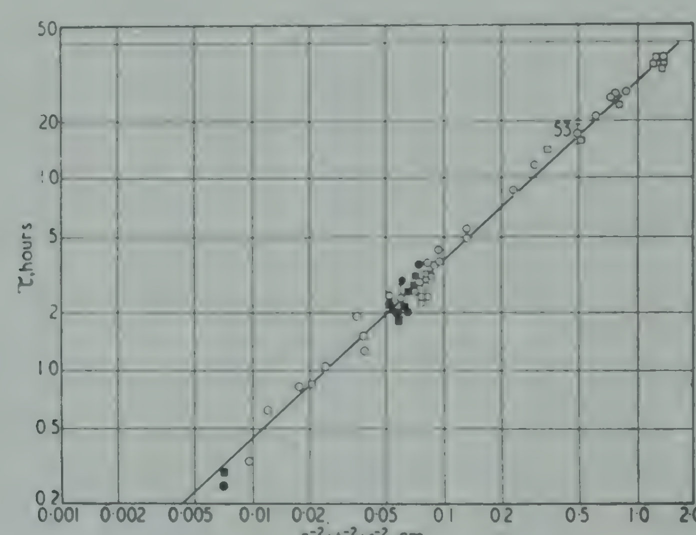

FIG. 21. *Drying time-constant, τ_i, as function of shape factor* ● $a>b, c$; ■ $b>a, c$; ○ $c>a, b$; □ $a=b=c$

The shape factor $(a^{-2} + b^{-2} + c^{-2})^{-1}$ may now be applied to normalize any set of results to a given thickness, and this procedure has been followed in constructing the histogram showing the distribution in values of τ_i in Fig. 20.

Directional effects

In order to determine whether or not cod muscle behaves as an isotropic medium, sets of thin sections cut parallel to the principal planes (Fig. 1) were dried under identical conditions, the individual sections in each set being cut from adjacent portions of a single fillet. The effective diffusion coefficients, D_x, D_y, D_z, parallel to each of the principal axes were then obtained from the slopes of the straight portions of the plots of log $(W_t - W_e)$ against t. The ratios D_x/D_z and D_y/D_z obtained from these values (Table IV) give an indication of the degree of anisotropy of the medium. There appears to be no significant difference between the mean values of the two ratios.

Taken together, the pooled mean of these ratios differs significantly from unity, the probability of the difference arising by chance being 3·8%. It is therefore concluded that the apparent diffusion coefficients parallel to the directions of the axes Ox and Oy are probably equal, and the value of each is about 10% less than the value of the diffusion coefficient parallel to the direction of the Oz-axis.

Table IV

Effective diffusion coefficients parallel to principal axes in cod muscle

Run Nos.	D_x, cm.²/sec.	D_y, cm.²/sec.	D_z, cm.²/sec.	D_x/D_z	D_y/D_z
92, 93, 94	3·34	2·74	3·37	0·991	0·813
98, 99, 100	2·53	2·98	3·49	0·725	0·854
101, 102, 103	2·79	3·38	3·91	0·714	0·864
104, 105, 106	3·36	3·78	3·61	0·931	1·047
159, 160, 163	3·54	2·99	2·96	1·196	1·010
165, 166, 167	2·53	2·78	3·16	0·801	0·880
Mean	3·02±0·45	3·11±0·40	3·42±0·34	0·893±0·035	0·911±0·009
				0·902±0·020	

Effects of air velocity and relative humidity

As might be expected, air velocity has no influence on drying during the falling-rate period, the correlation coefficient, r, between the drying time-constant and air velocity being −0·036 for the results shown in Fig. 22.

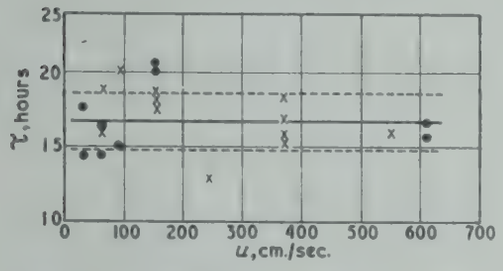

FIG. 22. *Effect of air velocity on drying time-constant, τ_i, at 30° of fillet piece 10 × 5 × 1·5 cm.*
○ 14·8% R.H.; × 30% R.H. Dotted lines indicate value 3 of standard deviation obtained from Fig. 20

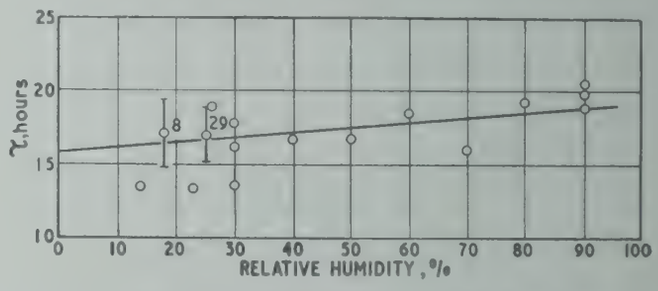

FIG. 23. *Effect of relative humidity on drying time-constant, τ_i, at 30° of fillet piece 10 × 5 × 1·5 cm.*

Equation (30) shows that the free water content at any time is a function of the difference between the initial and the equilibrium water content, but that the value of S in the exponent is not. It follows by differentiating equation (30) that the rate of drying depends on this difference and therefore on the relative humidity, since the equilibrium water content varies with relative humidity (Fig. 19). Its effect will, however, be negligible except when the relative humidity is very high because at the higher values the difference between the initial and the equilibrium water content changes rapidly with relative humidity. The drying time-constant ($\tau = 1/S$), on the other hand, will be independent of relative humidity unless the effective diffusion constant varies. Fig. 23 shows that τ_i appears to increase slightly with relative humidity, R ($r = +0{\cdot}342$, $N = 50$). The equation of the regression line is

$$\tau_i = 0{\cdot}0375R + 15{\cdot}7$$

for a cod fillet piece 10 × 5 × 1·5 cm. (τ_i in h.).

Effects of storage in ice and freezing

Fish is normally iced in the holds of fishing vessels to retard spoilage. Frequently the period of icing before the fish is landed at home ports is as much as 12 days or more. During this period the effects produced by bacteria and by autolytic enzymes bring about changes in the chemical composition and structure of the muscle tissue. These changes are accompanied by the formation of an expressible fluid, known as 'drip,' which increases in amount with the period of stowage in ice. In addition, a certain amount of leaching of soluble constituents takes place as the melt water flows over the fish. It might be expected therefore that the time of storage in ice would produce a variation in the drying properties of fish muscle. To establish the magnitude of the effect, if it exists at all, a series of experiments was carried out with fillet pieces 10 × 5 × 1·5 cm. cut from North Sea cod which had been iced for various periods of time and filleted immediately before drying. In these experiments fillets were cut from the flesh without previous freezing. The results, corrected for small variations in thickness, are given in Table V.

Table V

Values of drying time-constant, τ_i, for cod fillet pieces stored in ice for various periods of time
Size of fillet pieces 10 × 5 × 1·5 cm.
Air temperature 30°C.

Run No.	Days in ice	Drying time-constant, h.
8A	1	13·2
9A	1	18·8
195A	2	15·0
10A	4	13·3
11A	8	16·6
12A	12	17·7

The correlation coefficient for these figures is −0·088 and there is therefore no perceptible relationship between drying time-constant and storage time in ice. For this reason it was unnecessary to ensure that all the fish was of uniform freshness in any of the experiments described here.

The mean value of the drying time-constant for these six results (15·8 ± 2·3 hours) is not significantly different from the mean value (16·71 ± 1·87) for all 53 determinations represented in Fig. 20. Of the latter, 47 values were obtained for fillet pieces cut from cod which had been frozen and stored at −30°C for periods of up to one year. It may therefore be concluded that freezing and storage under these conditions has no perceptible effect on the drying of subsequently thawed fish fillets.

Effect of temperature

In all processes of non-gaseous diffusion and in all condensed media, the rate of flow of the diffusing substance is observed to have a positive temperature coefficient, but in biological materials and other substances in which an increase of temperature is accompanied by structural and chemical changes, this behaviour is modified.

Fish muscle is in several respects very heat-labile. At temperatures exceeding about 30°, denaturation of the proteins takes place, the process becoming increasingly rapid as 100° is approached. In addition, both the structure of the cells and the composition of the cell constituents are considerably affected. Unless these factors have no influence on the diffusion of water in the muscle, the effects of structural and chemical changes will be evident in addition to the purely kinetic effects which would otherwise predominate.

Experiments to determine the variation with temperature of the effective diffusion coefficients, D_i and D_{ii}, presented certain difficulties. First, the drying time necessary to estimate D_{ii} to an accuracy approaching that of D_i from the drying curves of fillet pieces of the thickness normally used (1·5 cm.) was of the order of several weeks at room temperature or below. Second, since it was not convenient to cool the wind tunnel artificially to obtain the lower temperatures, the laboratory heating had to be turned off when sufficiently cold weather occurred, in the hope that its duration would be adequate to complete the run. Third, although in this way controlled temperatures down to 10° were achieved, it was often very difficult to maintain constant humidity. Fourth, the obvious expedient of using thinner fillet pieces was of limited value because, owing to the effects of cooling already considered, the errors involved in determining D_i, which became more pronounced as the air temperature increased, could not be neglected for fillet pieces thinner than 1·5 cm. Consequently, in order to avoid prolonging the already considerably protracted period of time necessary to obtain data, D_i was obtained from the drying curves of 1·5 cm. thick fillet pieces while D_{ii} was principally obtained from the curves of those 0·5 cm. thick.

The logarithms of these values of D_i and D_{ii} are plotted against the reciprocal of absolute temperature, T, in Fig. 24 (lines A and B) together with the few results available for D_{ii} obtained from the drying curves of 1·5-cm.-thick fillet pieces (line C). To illustrate the effect of cooling thin samples, the line representing the variation of D_i with $1/T$ obtained with 0·5-cm.-thick fillet pieces is shown broken (line D): experimental points are omitted for clarity. Each set of results, except the last, may be represented by an Arrhenius type of relationship which is of the form

$$D_e = D_o \exp(-E/RT) \quad \ldots\ldots (35)$$

where D_o is a constant, E is the energy of activation for diffusion and R is the gas constant.

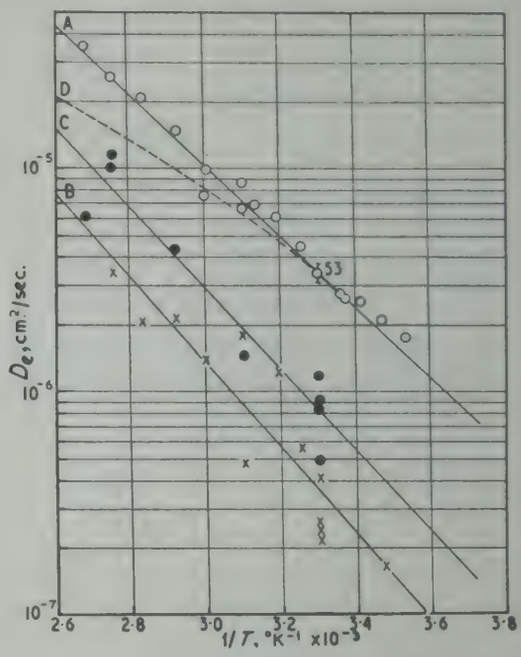

FIG. 24. *log* D_i *and log* D_{ii} *as function of reciprocal of absolute temperature for cod muscle*
Line A: log D_i for fillet pieces 10 cm. × 5 cm. × 1·5 cm.;
Line B: log D_{ii} for fillet pieces 10 cm. × 5 cm. × 0·5 cm.;
Line C: log D_{ii} for fillet pieces 10 cm. × 5 cm. × 1·5 cm.;
Line D: log D_i for fillet pieces 10 cm. × 5 cm. × 0·5 cm.

In order to test how well this relationship represents the data presented in Fig. 24, the correlation coefficient, r, between log D_e and $1/T$ was calculated for each set of results represented by lines A, B and C. The line of best fit was obtained from the regression line in each case: this gives the best values of D_o and E/R. Table VI gives values of r, D_o and E/R obtained in this way. Values of E are also tabulated.

It is seen at once that the correlation is very high between log D_i and $1/T$ and between log D_{ii} and $1/T$ and that the slopes of lines A and B differ significantly. The differences between the results represented by the two lines B and C are difficult to interpret owing to the paucity of the latter results.

Table VI

Values of r and best values of D_o, E/R *and* E *for cod muscle*

	1st phase, 1·5 cm. *Line A*	2nd phase, 0·5 cm. *Line B*	2nd phase, 1·5 cm. *Line C*
r	0·975	0·935	0·951
D_o, cm.²/sec.	0·54	0·74	0·77
E/R, °K^{-1}	3620 ± 100	4420 ± 610	4170 ± 510
E, cal./mol.	7190 ± 200	8780 ± 1200	8280 ± 1010

The relatively broad scatter of the points about line B does not permit the values of D_o and E/R to be determined for the second phase of the falling-rate period with the same precision as the corresponding values for the first phase. It can be concluded, however, that while the two values of D_o do not differ significantly, the activation energy in the second phase is significantly greater than in the first phase. The meaning of these results will be considered in relation to other observations in the discussion. There are no obvious effects resulting from the temperature-labile nature of fish muscle, such as would be indicated by changes of slope or discontinuities in either of the lines A or B, so that unless these effects result in an exponential dependence of D_i and D_{ii} on $-1/T$, the results suggest that structural and chemical changes in the medium have no influence on the diffusion of water through it.

Drying behaviour of various species

The rate of evaporation from the cut surfaces of all species of fish studied corresponded closely to that for a saturated surface during the constant-rate period, as was shown for cod. During the falling-rate period each of the species so far studied has shown the same characteristic drying behaviour as was observed for cod, namely an initial, fairly rapid, exponential decrease of the free water content followed by a second, very slow, exponential decrease. Table VII gives the effective diffusion constants D_i and D_{ii} at 30° C for a number of species of fish. With the exception of the values given for cod, the results relate to single determinations. Also

Table VII

Values of D_i and D_{ii} at 30°C for various species of fish

Species	Fat content (% of wet weight)	D_i (10^{-6} cm.²/sec.)	D_{ii} (10^{-6} cm.²/sec.)
Catfish (*Anarrhichas lupus*)	0·102	3·61	0·795
Cod (*Gadus callarius*)	~0·05	3·40 ± 0·36*	0·81 ± 0·04†
Conger eel (*Conger conger*)	3·766	2·28	0·425
Dab (*Pleuronectes limanda*)	0·460	2·94	0·52
Dogfish (*Acanthius vulgaris*)	8·60	0·83	0·15
Haddock (*Gadus aeglefinus*)	0·105	3·25	~0·6
Halibut (*Hippoglossus vulgaris*)	0·208	2·49	0·58
Lemon sole (*Pleuronectes microcephalus*)	0·094	2·63	~0·4
Ling (*Molva molva*)	0·047	3·57	0·54
Mackerel (*Scomber scombrus*)	0·694	2·21	0·35
Monkfish (*Lophius piscatorius*)	0·094	3·06	~0·4
Saithe (*Gadus virens*)	0·111	3·06	~0·3
Skate (*Raia batis*)	0·139	3·28	1·03
Whiting (*Gadus merlangus*)	0·036	2·72	0·48

The common and scientific names for the species given are those according to the *International Fish Journal*.[16]

*Mean and standard deviation of 53 determinations.
†Mean and standard deviation of 9 determinations.

tabulated are the values for the fat content of each sample. The Table shows that the value of D_i is approximately the same for each species of non-fatty fish (fat content less than about 0·1 %); and that, for the fatty fish, a high fat content corresponds to a low diffusion coefficient. Similar observations apply to D_{ii} values which are in general approximately one-fifth of the D_i values irrespective of fat content.

Shrinkage

In the foregoing it has been tacitly assumed that shrinkage of muscle does not occur during drying, and the effective diffusion constants have been calculated on the basis of the initial dimensions, but shrinkage does in fact take place in the direction of each of the three principal axes, as shown in Fig. 25. The effect is most pronounced in the direction parallel to the z-axis and least pronounced parallel to the x-axis. Such shrinkage introduces a number of problems into the analysis of the results, some of which may be solved by the use of various artifices.

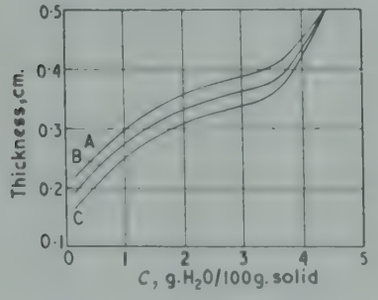

FIG. 25. *Relationship between mean water concentration and thickness measured at centre of cod fillet pieces initially* 4 × 4 × 0·5 cm.
Curve A: transverse section, thickness 2*a*;
Curve B: horizontal longitudinal section, thickness 2*b*;
Curve C: vertical longitudinal section, thickness 2*c*.

Danckwerts[17] has overcome difficulties inherent in applying the equations of diffusion to shrinking systems by allowing the co-ordinate system to shrink with the non-aqueous material of the specimen. In this co-ordinate system ' pseudo ' dimensions, denoted by the symbol ψ, are introduced, in which ψ-volume has the dimensions of mass, ψ-area the dimensions of $(\text{mass})^{2/3}$ and ψ-thickness the dimensions of $(\text{mass})^{1/3}$, each being related to the dry weight of the specimen. It is shown that where the conditions are such as to allow the diffusion coefficients to be considered constant, the ' proper ' diffusion coefficient is related to the ψ-diffusion coefficient by the expression

$$D_{(\text{proper})} = \frac{D_\psi}{\rho_n^{2/3}} \qquad \ldots\ldots (36)$$

$$\text{where } \rho_n = \frac{\text{weight of non-aqueous material}}{\text{' proper ' volume of system during experiment}}$$

It is self-evident that the rate of transfer of water through the containing surfaces is at all tim e identical in both systems.

It is an experimental fact that the average concentration of free water in a sample of fish muscle decreases exponentially with time (except for small values of time) in accordance with the solution of the diffusion equation given in equation (27), without making any assumptions as to dimensions. If the necessary transformations are made, a similar solution is obtained and D_ψ may be derived directly by experiment. Since, however, it is observed that D_ψ is constant over a wide range of initial shape and subsequent shrinkage, it is possible to convert D_ψ to $D_{(\text{proper})}$ at any arbitrary value of this ' proper ' volume. It is convenient to choose this to be the initial volume so that the diffusion can be characterized by $D_{(\text{proper})}$ related to the initial dimensions. This value of $D_{(\text{proper})}$ then corresponds to D_e derived from the experimental results when shrinkage is ignored.

The apparent invariance of D_e during the first and second phases of the falling-rate period therefore enables the drying behaviour to be calculated for a sample of any given initial dimensions, ignoring variations in the ' proper ' volume during drying. If this procedure were not valid, values of D_e would be expected to vary considerably with the shape and size of the fillet piece. Fig. 21 shows that when the effective diffusion constant during the first phase of the falling-rate period (i.e., when $D_e = D_i$) is considered, the effect of such variation of shape and size is not apparent, otherwise the results could not be represented by equation (32). Further evidence in favour of the invariance of D_i is adduced from the drying curve obtained when the drying of a sample is interrupted, the water is allowed to equilibrate and the drying is then resumed under the same external conditions. If the true value of D_ψ were to change significantly with concentration, then its apparent value after equilibration would be expected to change. That such change is small or non-existent is shown in Fig. 26 in which the slopes of the straight portions of the plot of the logarithm of free water against total drying time are nearly the same. Thus, the slope of these two lines in terms of ψ-quantities is $\pi^2 D_\psi\ (a_\psi^{-2} + b_\psi^{-2} + c_\psi^{-2})/4$, indicating that D_ψ remains constant since, by definition, the ' pseudo ' dimensions $2a_\psi$, $2b_\psi$, $2c_\psi$ of the fillet piece remain unchanged.

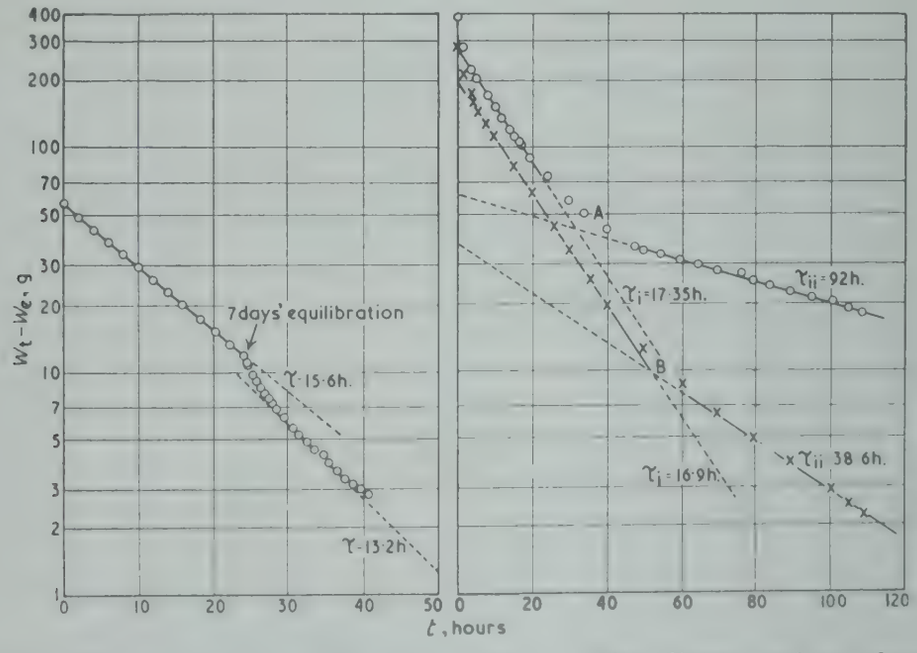

FIG. 26. *Effect of interrupted drying on subsequent drying characteristics*
Cod fillet piece 10 × 5 × 1·45 cm. dried at 30° and 50% R.H. for 24 hours, water allowed to equilibrate for 7 days, and drying resumed as before.

FIG. 27. *Effect of brining on drying characteristics of cod muscle at* 30°
Curve A, for 6 fillet pieces 10 × 5 × 1·49 cm. before brining for 1 hour in saturated solution of sodium chloride; Curve B, for 5 fillet pieces 10 × 5 × 1·46 cm. unbrined.

The possibility remains that a combination, fortuitous or otherwise, of the effects of shrinkage and concentration-dependence of diffusion could give rise to an apparently constant D_ψ. Unfortunately it is impossible to decide, on the basis of the data relating to the first phase of the falling-rate period, whether such a combination occurs, but the data for the second phase

show that D_{ii} remains constant even though shrinkage is negligible for large relative changes of water concentration. This suggests that the effective diffusion constant is not concentration dependent during the second phase.

Miscellaneous effects

It is well known that brined fish takes considerably longer to dry than unbrined fish, but the reason for this behaviour is not at all clear. The effect is illustrated in Fig. 27, where the logarithm of the weight of free water is plotted as a function of time for brined cod muscle (curve A) and for unbrined muscle (curve B). Initially, both curves are characterized by almost the same slope, the effective diffusion coefficients at 30° being $3{\cdot}09 \times 10^{-6}$ and $3{\cdot}23 \times 10^{-6}$ cm.^{2} sec. respectively. The drying curve for the brined samples enters the second phase of the falling rate period considerably sooner than is the case for the unbrined samples and the effective diffusion coefficients become $0{\cdot}61 \times 10^{-6}$ and $1{\cdot}35 \times 10^{-6}$ cm.^{2}/sec. for brined and unbrined samples respectively. In the example illustrated in Fig. 27 the time taken to dry the samples to 4% water content relative to dry weight would have been 530 hours for the brined muscle and only 88 hours for the unbrined muscle.

Although an investigation of the phenomenon of drying retardation due to brining is not within the scope of the present paper, it may be seen from the above example that the two principal factors which appear to contribute to retardation are, firstly, an early entry into the second phase of the falling-rate period and, secondly, in this one experiment, a considerably smaller diffusion constant than for unbrined muscle during this phase.

Among the possible causes of the observed behaviour is the effect of denaturation of the proteins by the salt or the formation of protein–salt complexes, both of which considerably affect the structure of the medium and might be expected to modify the diffusion rate. Evidence which might be relevant to the hypothesis of denaturation comes from measurements of the diffusion constants in fish muscle in which the protein has been denatured (*a*) by cooking and (*b*) by previous drying and reconstitution before re-drying.

Fig. 28 shows that cooking results in an initial phase of rapid drying, in which the effective diffusion constant at 30° is $9{\cdot}2 \times 10^{-6}$ cm.^{2}/sec., followed by a second phase in which the diffusion constant is $0{\cdot}36 \times 10^{-6}$ cm.^{2}/sec. The former is 2·7 times as great as the normal value of D_i at this temperature and the latter is about the usual value of D_{ii}, so that in this case cooking has a pronounced effect on drying behaviour during the first phase, but no significant influence during the second phase. The abnormally high value of D_i is probably due to the introduction of porosity in the muscle as a result of cooking. The usual logarithmic plot of free water against time for a sample of cod muscle dried at 30° is shown in Fig. 29 together with a similar plot for the same sample dried under the same conditions after being reconstituted.

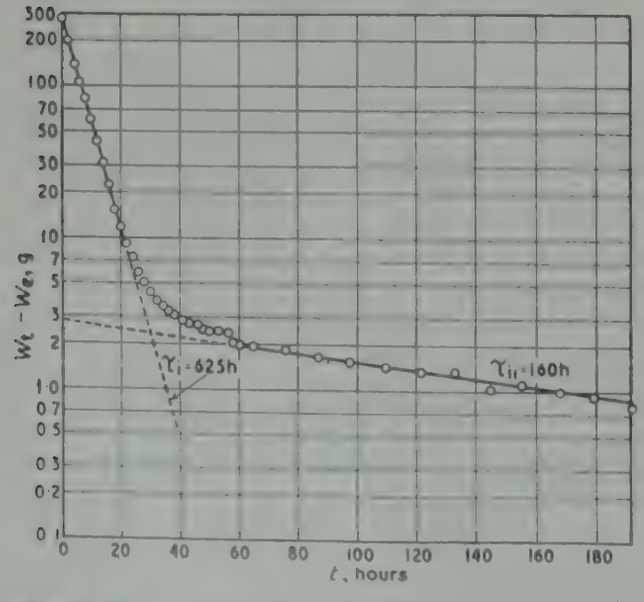

FIG. 28. *Effect of cooking on drying characteristics at 30°*
Five cod fillet pieces 10 × 5 × 1·51 cm. steamed for 40 min. before drying.

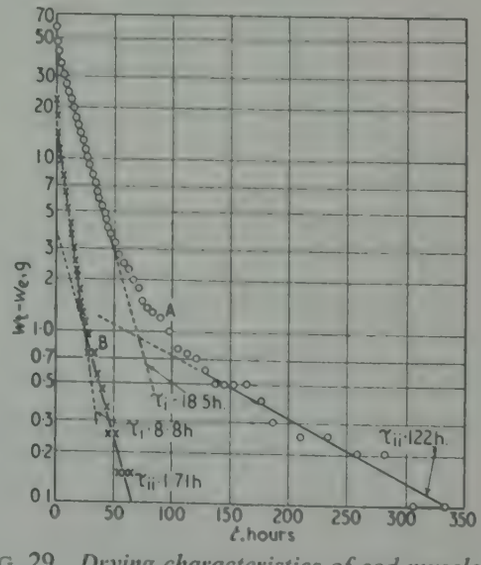

FIG. 29. *Drying characteristics of cod muscle before and after reconstitution*
Curve A, initial drying behaviour; Curve B, drying behaviour after reconstitution. Single fillet piece 10 × 5 × 1·52 cm dried at 30°.

The value of D_i after reconstitution is 2·1 times as great as the corresponding value before reconstitution, during the first period, a similar effect to that due to cooking. D_{ii} after drying and reconstitution is, however, very close to the mean value of D_i observed during normal drying at the same temperature. Furthermore, there is no evidence of the effective diffusion constant falling off to the usual value of about $0{\cdot}3 \times 10^{-6}$ cm.²/sec. as the water content of the system approaches its equilibrium value.

It is clear therefore that the physical changes in the medium, which give rise to retardation of drying after fish muscle has been brined, are different from those changes brought about either by cooking or by previous drying.

Discussion

In the foregoing it has been assumed that water migrates within fish muscle by a process of diffusion. Experimental evidence which strongly supports this assumption includes the exponential form of the drying curve in the falling-rate period, the approximate proportionality between the drying time-constant, τ_i, and the shape factor $(a^{-2} + b^{-2} + c^{-2})^{-1}$, the lack of correlation between τ_i and air-velocity and the Arrhenius type temperature dependence of calculated values of the effective diffusion constants D_i and D_{ii}. No assumption has been made, however, as to the particular type of flow mechanism giving rise to the observed behaviour. To obtain some indication of the mechanism(s) most likely to operate, it is appropriate to consider the experimental evidence in relation to the following possible processes:

(1) Capillary flow of liquid water;
(2) Viscous flow of water vapour;
(3) Thermal diffusion;
(4) Surface diffusion in a porous medium;
(5) Gaseous diffusion;
(6) Molecular diffusion in a solid medium.

Those processes relating to flow through a capillary or porous structure may be excluded by virtue of the structure of the fish muscle both in the native state and when partly dried. Visual examination of muscle sections at various stages of drying reveals a continuous gel structure completely free of pores or capillaries. Measurements of the ' true ' density of dried fish muscle by means of a gas voluminometer[6] using air, hydrogen and oxygen show no noticeable difference in the values obtained with each of the gases, as might result if there were to exist an extensive capillary or micro-pore structure. A capillary structure, if it exists at all, would be orientated parallel to the muscle fibres (i.e., principally along the length of the fish) and the resultant flow would be pronounced in this direction. Observations of directional effects show that the medium is almost isotropic with a slightly greater flow in a direction at right angles to the general direction of the muscle fibres.

It may be shown[18] that the flow of gases in a capillary or porous system, characterized by a permeability coefficient B, is similar to that observed in diffusion through a solid medium. B has the dimensions cm.²/sec. which are the same as those of a diffusion coefficient, but since for theoretical reasons B varies with $1/T$ and not with $\exp(-1/T)$ as observed, this possibility must be excluded.

Simple kinetic theory for gaseous diffusion gives the relationship between the diffusion coefficient D, the mean thermal velocity $\bar{v}$ and the mean free path λ as

$$D = \tfrac{1}{3}\bar{v}\lambda \qquad \ldots\ldots (37)$$

But since v is proportional to $\sqrt{T}$, the temperature coefficient is again different from the experimental value.

The hypothesis of thermal diffusion (Soret effect) is rejected because the effect is negligible for the small temperature gradients which obtain during the falling-rate period. Furthermore, reversal of temperature gradients at the surface were not observed to lead to reversal in the direction of flow of water in fish muscle.

The remaining hypothesis, that of molecular diffusion, involves random walk behaviour such as would occur in any of the following processes:

(1) Migration of holes in a lattice containing vacancies.
(2) Migration of interstitial molecules in a lattice.
(3) Interchange between molecules on normal lattice sites and those on interstitial sites.
(4) Surface migration of adsorbed molecules.

It is not very easy to distinguish between any of these processes experimentally since for each

of these models an essentially similar form of expression is obtained for the coefficient of diffusion. The reason is that a particle moving from one equilibrium position to an adjacent one migrates on a potential surface with a saddle point between the original and final sites.[19] It may be shown on the basis of an elementary theory of diffusion in solids[20] that if n_v is the number of vacancies present per cubic centimetre and n_n is the number of nearest neighbours of a vacancy, then the number of particles per cubic centimetre free to surmount a barrier of energy U (per mole) will be

$$n_f = n_v n_n \exp(-U/RT) \quad \ldots\ldots (38)$$

where $$n_v \simeq n \exp(-E_v/RT) \quad \ldots\ldots (39)$$

E_v is the energy necessary for the formation of vacancies equivalent to one mole and n is the number of particles per cubic centimetre. The diffusion coefficient may then be shown to be

$$D \simeq \frac{d^2\nu}{3} \exp(-E/RT) \quad \ldots\ldots (40)$$

where $E = U + E_v$, d is the distance between nearest neighbours in the lattice and ν is the vibration frequency of a particle in the lattice given by

$$\nu = kT/h \quad \ldots\ldots (41)$$

k being Boltzman's constant and h Planck's constant.

In equation (35) D_o corresponds to the frequency factor $d^2\nu/3$ and E corresponds to the activation energy for diffusion.

Writing $$D_o \simeq \frac{d^2kT}{3h} \quad \ldots\ldots (42)$$

and inserting the appropriate observed values of D_o from Table VI, it is found that $d \simeq 10^{-6}$ cm. for fish muscle for both the first and second phases of the falling-rate period.

The transition from the first phase to the second phase may be characterized by the point of intersection of the two straight lines drawn in the plot of the logarithm of free water against time. This point of intersection, which for convenience will be called the transition point, will give a rough indication of the value of the mean water content at which the transition takes place. This value will, however, be very approximate and possibly somewhat higher than the true value locally within the sample since at different times varying proportions of the sample will be subject to the conditions obtaining in each phase. Values of the mean water concentration $\bar{W}_p$ at the transition point, expressed as weight of water per unit weight of non-aqueous material, are presented in Table VIII for the ranges of temperature and humidity conditions investigated. In computing these values it was assumed that the water relations curve for fish muscle (Fig. 19) varies only slightly with temperature. $\bar{W}_p$ was then obtained by adding the equilibrium water content corresponding to the appropriate value of relative humidity to the free water content deduced from the weight of free water indicated by the transition point. It is seen that all values of $\bar{W}_p$ lie between about 0·10 and 0·15 for temperatures between 15° and 60°C. That the values of $\bar{W}_p$ are less than 0·10 for temperatures in excess of 60°C may perhaps be associated with errors involved in deriving the equilibrium water content at these higher temperatures.

Table VIII

Mean water concentration at transition point for cod muscle

Run No.	Temperature, θ °C	Relative humidity, %	$\bar{W}_p$, g.H_2O/g. solid
45B	50	25	0·119
48B	30	40	0·145
49B	35	25	0·140
50B	50	25	0·108
56B	60	25	0·143
57B	30	32	0·151
62B	15	~40	~0·15
64B	80	6	0·085
66B	70	~10	~0·08
67B	90	< 6	~0·06
86A	30	30	0·110
88A	30	30	0·102

In order to understand the nature of the transition between the two phases it is necessary to consider the adsorption properties of cod muscle in the near-dry state by examining the water relations curve shown in Fig. 19. This has the appearance of a Type-II adsorption isotherm, one of the five types of isotherm for which Brunauer[21] has put forward a multimolecular adsorption theory for adsorption taking place on a free surface. The theory relates the total volume v of gas adsorbed at relative pressure p/p_o (where p is the pressure and p_o is the saturation vapour pressure) to the volume v_m of gas adsorbed when the entire adsorbent surface is covered with a complete unimolecular layer, by the equation

$$\frac{p}{v\,(p_o - p)} = \frac{1}{v_m C} + \frac{C-1}{v_m C} \cdot \frac{p}{p_o} \quad \ldots\ldots (43)$$

C is a constant given by the equation

$$C = \exp\,(E_m - E_l)/RT \quad \ldots\ldots (44)$$

E_m being the heat of adsorption of the first layer and E_l the heat of liquefaction.

If the assumptions made by Brunauer are held to be valid for the surfaces of protein molecules in fish muscle, the isotherm equation may then be applied to the data plotted in Fig. 19. These data are represented in Fig. 30 in which $p/v(p_o - p)$ is plotted against p/p_o. The intercept of the straight line drawn through the points is $1/v_m C$ and the slope is $(C-1)/v_m C$. From these values the two constants for cod muscle are found to be

$v_m = 110$ c.c. of water vapour per g. of solid;* $C = 7{\cdot}59$ at 30°C,

whence the water concentration W_m corresponding to the adsorption of v_m c.c. of water vapour per g. of solid is $0{\cdot}088 \pm 0{\cdot}009$ g. of water per g. of solid, and $E_m - E_l$ is 1220 ± 170 cal. per mol. The straight-line relationship observed in the isotherm plotted in Fig. 30 supports the assumption of multimolecular adsorption of water on the surfaces of the protein molecules and is consistent with the process of surface migration of adsorbed molecules suggested earlier [process (4)] as a possible diffusion mechanism.

If now the values of W_m and $\bar{W}_p$ are compared, it will be seen that the latter values are generally higher, but when it is remembered that $\bar{W}_p$ probably over-estimates the true value, W_p, of the water concentration at which the transition occurs, the possible identity of W_m and W_p is not incompatible with the experimental results. Such an identity is plausible if it is assumed that the transition point is associated with the uncovering of the unimolecular layer of water after the outer layers have been removed.

On the basis of this assumption, an energy-level diagram for the processes of monolayer adsorption, diffusion and evaporation may be constructed (Fig. 31). According to the diagram,

$$E_m - E_l = E_{ii} - E_i \quad \ldots\ldots (45)$$

E_i being the activation energy for diffusion of molecules in the second and higher adsorbed

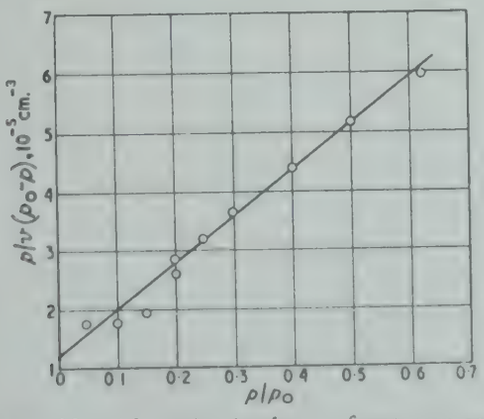

FIG. 30. *Adsorption isotherm of water on cod muscle at* 30°

Plotted according to straight-line equation (41) of multimolecular theory of adsorption[21]

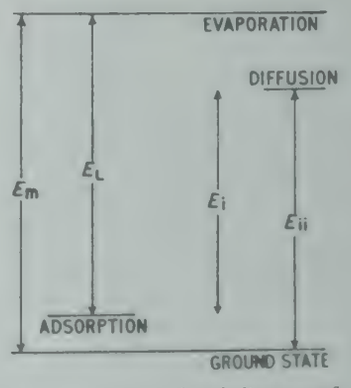

FIG. 31. *Energy-level diagram for diffusion and evaporation of water*

*The magnitude of this value strongly suggests that the unimolecular layer of water is bound mainly to the polar groups on the surfaces of the protein molecules; the remainder of the area of these surfaces is known to be hydrophobic.

layers and E_{ii} the activation energy for diffusion of molecules in the first layer. E_i and E_{ii} correspond to the experimental values of E given in Table VI for the first and second phases of drying represented by the lines A and B in Fig. 24. Owing to the large uncertainty in the estimated value of E_{ii} it is unfortunately not possible to test this hypothesis quantitatively and further work is indicated.

It is of interest to compare the value of E_{ii} for cod muscle with the value of the energy of activation (9800 ± 300 cal. mol.) of water migrating by surface diffusion along molecular fibrils in starch gel of very low water content given by Fish,[22] who suggests that this value is consistent with the breakage of two hydrogen bonds in order to attain the activated state of a water molecule. The agreement between the values of the activation energies for cod muscle and starch gel therefore suggests that a similar process occurs in the diffusion of water through fish protein gels.

Surface migration along the protein molecular fibrils appears to be a likely mechanism for the movement of water molecules, because (i) X-ray and electron microscope studies with living and dried muscle and muscle proteins[23] have shown that the repeat distance in the structure is unaffected by drying, and (ii) the structure of the protein fibrils is known to be very stable up to temperatures in the region of 100°, increasing temperature resulting merely in a slight unfolding of the fibrils. Assuming that the repeat distance is related to the distance between nearest neighbours on lattice sites, it is clear that both D_i and D_{ii} will be unaffected by gross shrinkage of the muscle, and that the Arrhenius-type relationship for these quantities will be unaffected by various forms of structural change brought about by heating the muscle. These features appear to have been confirmed by the experimental evidence already presented.

On the basis of the assumption that the process of diffusion of water in fish muscle may be characterized by an effective diffusion constant in an isotropic medium, it will now be shown that the duration of the constant-rate period can be predicted from the rate of evaporation per unit area, the effective diffusion constant, the dimensions of the sample and the free water concentration.

As in the solution of the equation for the diffusion of moisture within a solid, the analysis of the conditions at the surface during the constant-rate period may be considered as analogous to that of heat transfer.

Consider the free water concentration $C_x - C_e$ at any point x in the region $0<x<c$ in a slab of material with an initial free water concentration $C_0 - C_e$ out of which a constant flux ε passes at $x = c$. $C_x - C_e$ is given as

$$C_x - C_e = (C_0 - C_e) - \frac{\varepsilon c}{D}\left\{\frac{Dt}{c^2} + \frac{3x^2 - c^2}{6c^2} - \frac{2}{\pi^2}\sum_{n=1}^{\infty}\frac{(-1)^n}{n^2}\exp\left(-\frac{Dtn^2\pi^2}{c^2}\right)\rightarrow \cdot \cos\frac{n\pi x}{c}\right\} \quad \ldots\ldots\ldots\ldots\ldots (46)$$

provided there is no flow over $x = 0$.[23, 24] The suffix x has been dropped from D_x for convenience. D is assumed to be constant for all values of C_x, x and t.

If the free water concentration at the surface is $C_s - C_e$, then for $t>0$, $C_x - C_e = C_s - C_e$ at $x = c$, and equation (46) becomes

$$C_0 - C_s = \frac{\varepsilon c}{D}\left\{\frac{Dt}{c^2} + \frac{1}{3} - \frac{2}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp\left(-\frac{Dn^2\pi^2 t}{c^2}\right)\right\} \quad \ldots\ldots\ldots\ldots\ldots\ldots (47)$$

Now equation (47) breaks down when the rate of diffusion of water from the interior of the slab cannot maintain a sufficient flow to the surface. When this occurs, the saturated condition of the air at the surface can no longer be supported and the concentration of water at the surface of the slab rapidly diminishes towards its equilibrium value. The termination of the constant-rate period is therefore indicated when, at $t = t_c$ and $x = c$,

$$D(\partial C_x/\partial x) < \varepsilon.$$

This condition is then represented by equation (47) when the following values are inserted:

$$C_s = C_e;\ D = D_i;\ t = t_c.$$

Rearrangement gives the following expression for the rate of evaporation per unit area:

$$\varepsilon = \frac{D_i(C_o - C_e)}{c} \Big/ \left\{ \frac{D_i t_c}{c^2} + \frac{1}{3} - \frac{2}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{n^2\pi^2 D_i t_c}{c^2}\right) \right\} \quad \ldots\ldots\ldots\ldots (48)$$

For any given set of conditions the relationship between ε and t_c may be derived by direct calculation or, more conveniently, with the help of the curve relating the dimensionless group $D_i t_c / c^2$ to

$$\frac{\varepsilon c}{D_i(C_o - C_e)} = \left\{ \frac{D_i t_c}{c^2} + \frac{1}{3} - \frac{2}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \cdot \exp\left(-\frac{n^2\pi^2 D_i t_c}{c^2}\right) \right\}^{-1}$$

(Fig. 32). The appropriate value for D_i is that corresponding to the mean temperature of the slab. This temperature will be approximately that of the surface, θ_s. D_i is then given by equation (35) after inserting values for the parameters given in Table VI, putting $T = 273{\cdot}1 + \theta_s$. Fig. 33 shows families of curves for cod muscle relating t_c to ε for various values of c at surface temperatures of 0°, 50° and 100°. $C_o - C_e$ has been taken as 0·80 g. water/cm.^{3}.

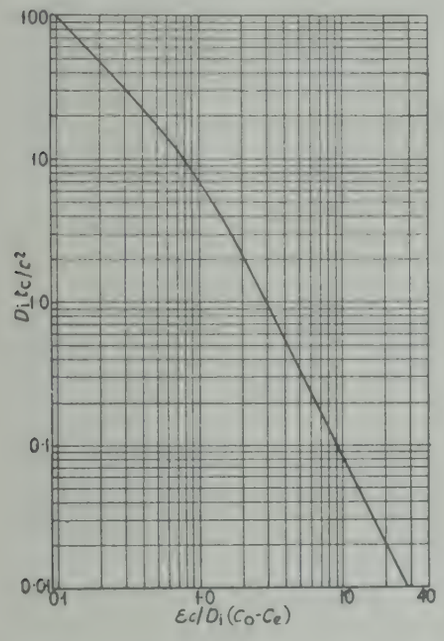

FIG. 32. Dit_c/c^2 *as a function of* $\varepsilon c/D_i\,(C_o - C_e)$

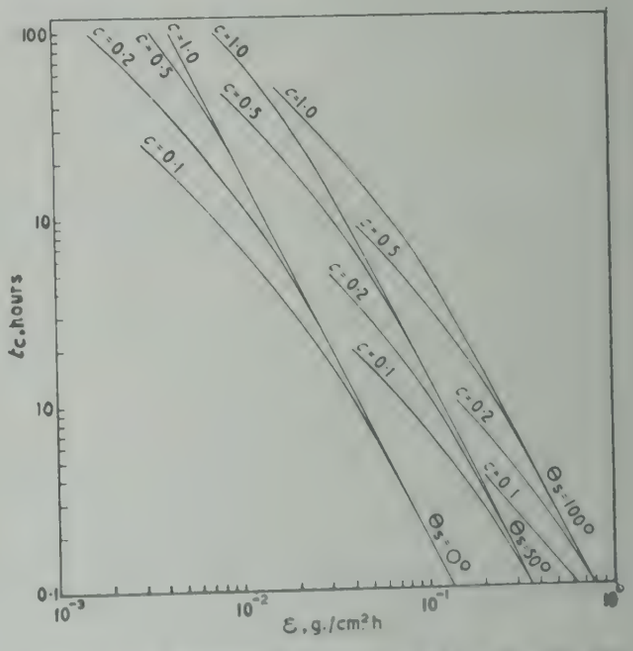

FIG. 33. *Relationship between* t *and* ε *at* θ_s = 0, 50, 100°C, *for cod muscle slabs of half thickness* c=0·1, 0·2, 0·5, 1·0 *cm.*

The theory has been extensively tested at 30°, for cod fillet pieces 0·5 cm. thick, dried under a variety of conditions of air velocity and wet-bulb depression. The results are represented in Fig. 34 in which t_c is plotted against the rate of drying per unit area corrected for geometrical effects as previously described. Theoretical curves are drawn for three values of surface temperature: 15°, 20° and 25°. These values were chosen to cover the range of surface temperature to be expected under the conditions of the experiments. Most of the results were derived for two values of wet-bulb depression, 8° and 12°, and for air velocities which varied from 30 to 549 cm. sec., so that a large proportion of the points would be expected to fall between the 20°- and 25°-curves.* An examination of Fig. 34 shows that for values of ε

*In all but four of the experiments the initial free-water concentration was in the range 0·79 to 0·81 g./cm.^{3}. The remaining four experiments were carried out at high relative humidities in order to achieve low rates of evaporation and, in consequence, the equilibrium water concentration was in each case greater than 0·2 g./cm.^{3}. Each result has therefore been corrected for this difference and is plotted in the figure together with the uncorrected value.

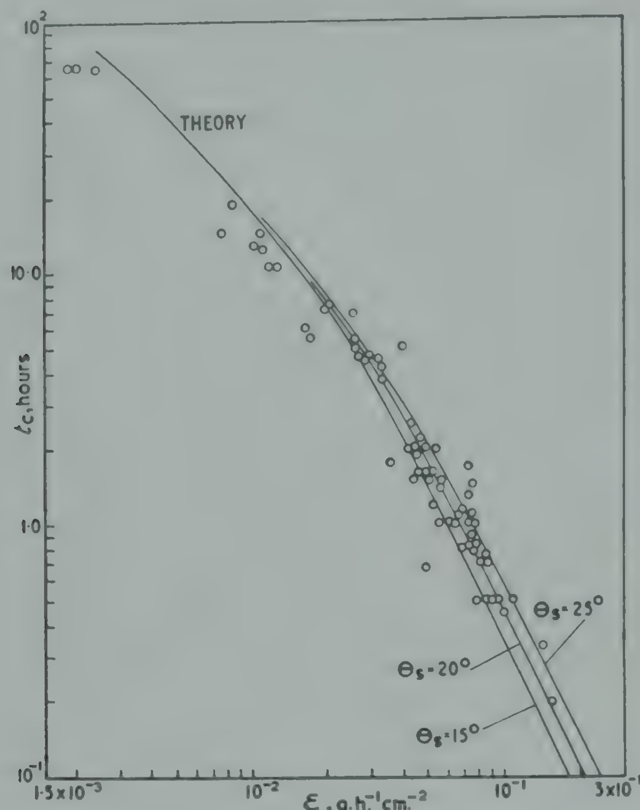

FIG. 34. *Effect of rate of evaporation on duration of constant-rate period at* $\theta_a = 30°$ *for cod fillet pieces* 0·5 *cm. thick, showing theoretical curves* $\theta_s = 15°$, 20°, 25°

O—O Result corrected to equilibrium water concentration of 0·15 g. H_2O/g. solid.

greater than 0·2 g./h. cm.², where these two curves diverge appreciably, about one-third of the number of points are in fact enclosed by these curves. Thus, having due regard for the errors involved in the determinations of t_c and ε, the agreement between experiment and theory is considered to be very satisfactory.

Equation (48) enables quantitative interpretations to be made of certain of the phenomena associated with the constant-rate period. Basic to each of these is the form of the variation of the local rate of evaporation, ε_x, along the length of the sample and the effect which this has on the local values of t_c. It is evident from Fig. 33 that, for high values of ε, t_c varies inversely with ε^2, so that according to equation (13) the local value of t_c is proportional to $(x/l)^{0\cdot 46}$. This therefore supports the assumptions made earlier that in zone 1 (i.e., where $0 < x/l < 0\cdot 2$) the local values of t_c are considerably less than those in zone 2 (i.e., where $0\cdot 2 < x/l < 1$), and that the mean rate of drying in zone 2 may be represented by the local rate at the centre of the surface, at which point the local value of t_c may be taken to represent the effective duration of the constant-rate period for the sample. The good agreement between theory and experiment shown in Fig. 34 confirms that these approximations are reasonable.

The variation of t_c with l (Fig. 13) follows from equations (10) and (48): ε decreases as l increases and so t_c increases with l in the manner observed.

The effects illustrated in Figs. 14 and 15, in which the duration of the effective constant-rate period decreases with increasing wet-bulb depression and air velocity, are also explained quantitatively by inserting the appropriate rates of evaporation into equation (48).

The mean water content, W_c, per g. of non-aqueous material, W_n, at $t = t_c$ is known as the critical moisture content[2] and is derived from the expression

$$W_c - W_n = \frac{W_o - \varepsilon A t_c}{W_n} \qquad \text{(49)}$$

where W_c is the weight of the sample at $t = t_c$ and W_n is the weight of non-aqueous material.

Conclusions

During the initial stages of drying, the rate of evaporation of water from the surface of fish muscle is constant and equal to that from a saturated surface of the same shape. The duration of this constant-rate period is related to the rate of evaporation per unit area, the effective diffusion constant, the dimensions of the sample and the free water concentration.

The form of the drying curve relating the weight of free water to time during the falling-rate period shows two distinct phases. The drying behaviour in the first phase is in accord with the solution of a diffusion equation based on Fick's Law. The results imply that the diffusion coefficient is constant and that its effective value is independent of shrinkage of the muscle. In the second phase the same considerations apply, the main difference being that the effective diffusion constant assumes a value which is less than that of the first phase: at 30°, for example, its value is approximately one-fifth of the latter.

The transition from the first to the second phase of the falling-rate period appears to be associated with the uncovering of the unimolecular layer of water which covers the protein molecules. The activation energy for diffusion is found to be greater in the second phase than it is in the first and the difference corresponds very approximately to the difference between the heat of adsorption of the monolayer and the heat of liquefaction of the water. If this is correct, then the processes of evaporation and diffusion may be characterized by a scheme of energy levels involving the heat of adsorption of the unimolecular layer of water, the heat of liquefaction of water and the energies of activation corresponding to each of the two phases of the falling-rate period.

During both the constant-rate and the falling-rate periods the drying behaviour of all species of non-fatty fish so far examined is identical. The effect of the presence of fat is to decrease the values of the effective diffusion constants in the first and second phases of the falling-rate period. One consequence of such a decrease in the former value is to reduce the duration of the constant-rate period.

Fish muscle is almost isotropic with respect to the diffusion of water. In cod muscle the effective diffusion coefficient in any direction parallel to the sagittal section is only about 10% less than that perpendicular to the plane of the sagittal section.

Brining of muscle results in an early transition from the first to the second phase in the falling-rate period. In the first phase the effective diffusion coefficient does not differ significantly from that for unbrined fish, but in the second phase the coefficient is considerably less than the corresponding value for unbrined fish. The combined effect of a short first phase and a very low effective diffusion coefficient in the second phase explains why salt fish takes considerably longer to dry than unbrined fish.

Acknowledgments

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Nomenclature

All quantities are in c.g.s. units

A = Surface area
B = Permeability coefficient
C = Concentration of water
D = Diffusion coefficient
E = Energy per mol.
E = Activation energy per mol. for diffusion
F = Shape factor
H = Heat
L = Latent heat of vaporization
N = No. of observations
O = Origin of system of rectangular co-ordinates
R = Relative humidity
R = Gas constant, $8{\cdot}314 \times 10^7$ ergs/mol.
S = Slope
T = Absolute temperature
U = Energy barrier per mol.
W = Total weight of system
a, b, c = Axial distances
e = Constant
d = Distance between nearest neighbours on lattice sites

f = Flux
h = Planck's constant, $6{\cdot}610\times10^{-27}$ erg/sec.
k = Boltzmann's constant, $1{\cdot}379\times10^{-16}$ erg/degree
k = Transfer coefficient
l = Length of surface measured parallel to air stream
l, m, n = Integers
p = Vapour pressure

Superscripts

$'$ $''$ = Intercept values on ordinate
$-$ = Mean value

Subscripts

a = Air
c = Constant rate
e = Equilibrium value
f = Free to surmount energy barrier
h = Heat
l = Liquefaction
m = Unimolecular layer
n = Nearest neighbour
n = Non-aqueous material
o = Initial value
o = Saturation value
p = Transition point
s = Surface
t = At a given time
v = Vacancy
r = Correlation coefficient
t = Time
u = Air velocity
v = Thermal molecular velocity
v = Volume
x, y, z = Displacements
ε = Rate of evaporation per unit area
θ = Temperature
λ = Mean free path
ν = Vibration frequency
τ = Drying time-constant
w = Mass
w = Wet-bulb
x = At x
x, y, z = In the direction of x, y, z, respectively
1 = Solid phase
2 = Liquid phase
i = First phase of falling rate period
ii = Second phase of falling rate period
ψ = Pseudo

Operators

cos = cosine
d = Differential
∂ = Partial differential
div = Divergence
grad = Gradient
∇ = Nabla, gradient
$\alpha, \beta, \gamma, \delta, \zeta$ = Constants

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Discussion

Dr. B. P. Fish: Perhaps I can suggest an explanation for the two apparent diffusion coefficients shown in your Fig. 18. Crank could never obtain anomalous drying curves by any diffusion coefficient which depended upon concentration. In the Appendix to my paper in this session, however, I have proposed a tentative theory for diffusion with a continuous temporal relaxation of the coefficient. Can I suggest that your D_i, D_{ii} may represent extreme values of a diffusion coefficient which decreases during the course of dehydration because of the stresses imposed on the material during this process? I see from your Table VII that the change in the diffusion coefficient is five-fold (a). The term ($a\tau$) in my equation (3 in the Appendix) corresponds to the negative time intercept (—55 h.) for the line of smaller gradient in your Fig. 18, from which I calculate a relaxation time (τ) of 11 h. Your curves intersect after 11 h. Has this any significance?

Dr. Jason: The temporal relaxation theory proposed by Dr. Fish certainly offers a very plausible explanation for the two apparent diffusion coefficients. The theory could be tested experimentally over a wide range of conditions by determining the quantities a, $a\tau$ and the time of intersection of the two curves for a number of thicknesses of sheet in order to evaluate τ. Unfortunately, most of the relevant data I have obtained for fish muscle dried at any given temperature relate to one thickness only. The following few results obtained at 30°C are of interest, however:

l, cm.	a	$a\tau$, h.	τ, h.	Time of intersection
0·502	9·15	42·5	4·65	5·2
0·510	7·44	39·0	5·25	6·0
1·44	3·46	138	39·9	49
1·76	2·18	132	60·5	104
1·92	2·31	170	73·5	90
2·50	1·96	132	68·7	123

It appears that a decreases rapidly with increasing thickness and that both τ and the time of intersection of the two curves increase with thickness. Only for thin sheets does the time of intersection appear to coincide with calculated values of τ.

The possibility still remains that the change in the diffusion coefficient results both from temporal relaxation and from a change in the activation energy as drying proceeds. The above results, however, do not provide a sufficient basis for the elucidation of this problem and further work is clearly called for.

Dr.C. L. Cutting (Humber Laboratory, D.S.I.R., Hull): Can it really be assumed that a kipper is a parallelepiped?

Dr. Jason: It obviously cannot be assumed that a kipper is a rectangular parallelepiped, although for approximate calculations the errors involved by taking the shape to be that of a thin slab of uniform thickness would not be very great. For more precise calculations for whole fish, split fish or fish fillets the effective thickness $2C_{eff}$ may be calculated by measuring the thickness $2C_i$ at r equally-spaced points in the plane of the sagittal section, thus

$$\frac{1}{C_{eff}} = \left(\frac{1}{r}\sum_{i=1}^{r}\frac{1}{C_i^2}\right)^{\frac{1}{2}}$$

The actual values assumed for the other two dimensions are not important provided that they are those of a rectangle of the same area and roughly the same dimensions as the sagittal section.

SOME PHYSICAL DATA CONCERNING THE DRYING OF POTATO STRIPS

By A. J. EDE

(Mechanical Engineering Research Laboratory, D.S.I.R., East Kilbride, Glasgow)

The designer of drying plant requires information on the rate of evaporation obtainable from the commodity to be dried, and on the effect upon it of various conditions of air-speed, temperature and so on. He will be familiar with the technique of calculating rates of evaporation from surfaces which are truly ' wet '; there is a close analogy between the rate of evaporation and heat transfer, the difference between the vapour pressure of water at the evaporating surface and that in the air stream corresponding to the difference between the temperature at the heated surface and that in the air stream. A further simplification may be possible: since in ordinary air-drying the latent heat of evaporation is supplied by the same air which carries away the evaporated water, it is unnecessary to consider in detail the conditions at the surface of the material being dried, as they are determined by the quality of the air. The rate of drying of a ' wet ' surface under such circumstances is approximately proportional to the difference between the dry- and wet-bulb temperatures of the air. It is possible, therefore, to use a drying coefficient, analogous to a heat transfer coefficient, based on the rate of evaporation divided by the wet-bulb depression of the air.

The drying of a solid material involves the passage of water from within the material to the surface either as a vapour or as liquid. In some cases this can proceed fast enough to impose no serious limitation on the rate of evaporation from the surface, which remains effectively ' wet.' In other cases the rate of flow of water to the surface is restricted and the rate of drying depends not only on the condition of the air but on the state of the material. This so complicates the problem that recourse must usually be had to direct experiment with the material under consideration.

This paper presents the results of a series of tests on the drying of potato, devised to obtain design data of the type referred to. Generally speaking, each test consisted of the drying of a sample of potato under constant conditions of air-speed and quality, the rate of evaporation being determined by periodic weighings. The results have been fully reported in D.S.I.R. Food Investigation Special Report No. 53 (London, H.M.S.O.), 1948; the present paper is in effect a condensed version of a part of that Report.

Drying of potato

It is evident that the rate of drying of a typical tray-load of material will be affected by many factors, such as the speed, temperature and humidity of the air stream, the size of the tray and the thickness of the layer of material, the size and water content of the individual pieces of material. It has, therefore, been possible to obtain only a general indication of the effect of each on the rate of drying.

It was first established that potato requires an impossibly long time to dry unless it is cut into comparatively small pieces. For example, a slice $\frac{3}{4}$ in. thick was not adequately dried after two days (Fig. 1).* The effect of size on the rate of drying of individual, separate strips is shown in Fig. 2, and it will be seen that the usual choice of strips of the order of $\frac{3}{16}$ in. to $\frac{1}{4}$ in. thick is a very reasonable one. The next few figures show further features of the drying of strips of about this size. Considering first an individual strip freely suspended in air, Fig. 3 shows how the rate of drying varies with time and with water-content. It is clear that there is no substantial period during which the rate of evaporation is constant and it may be inferred from this that for most of the time the rate of evaporation is significantly affected by the internal diffusion of water.

Fig. 4 shows the effect of the speed and wet-bulb depression of the air stream on the drying of single strips. At high water-contents both velocity and wet-bulb depression have a marked effect on the rate of drying. At low water-contents neither wet-bulb depression nor velocity have much effect, again presumably because the limiting factor is internal diffusion. At very

*The figures in this paper are reproduced by permission of H.M.S.O. They are taken from the D.S.I.R. report mentioned (now out of print).

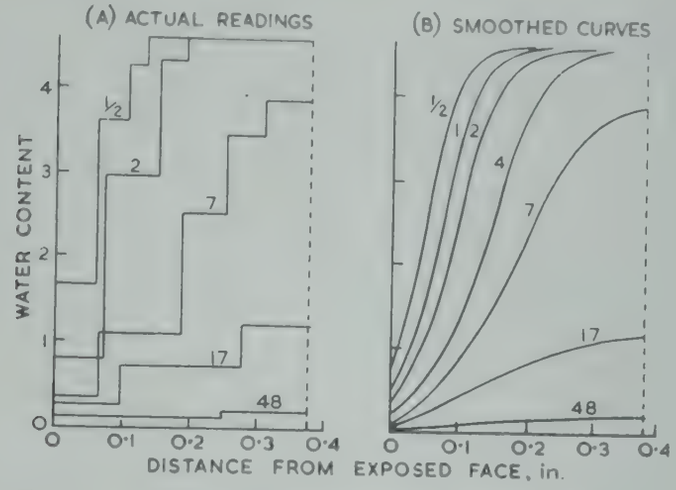

FIG. 1. *Gradient of water-content through $\frac{3}{4}$-in. slices of potato*

Dry-bulb 70°, wet-bulb depression 30°, speed 10 ft./sec.
Figures on curves are times in hours

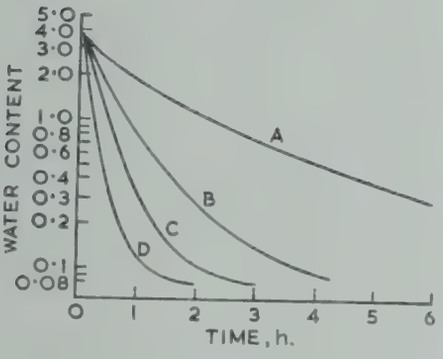

FIG. 2

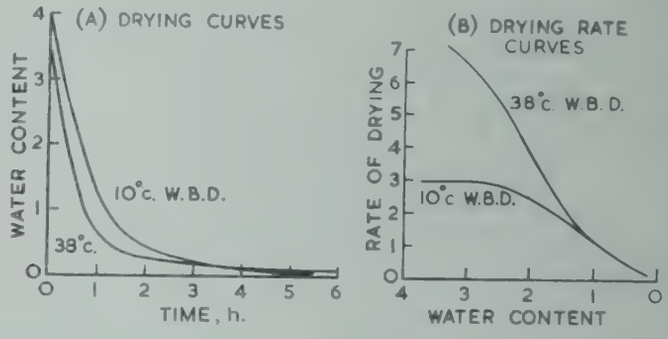

FIG. 3

FIG. 2. *Drying of individual strips of potato: effect of size of strip*

Dry-bulb 70°, wet-bulb depression 38°, speed 10 ft./sec.
Curve A $\frac{1}{2}$ in. × $\frac{1}{2}$ in. strips
Curve B $\frac{1}{4}$ in. × $\frac{1}{4}$ in. strips
Curve C $\frac{3}{16}$ in. × $\frac{5}{16}$ in. strips
Curve D $\frac{1}{8}$ in. × $\frac{5}{32}$ in. strips

FIG. 3. *Drying curves and rate curves for individual strips of potato, $\frac{1}{4}$ in. × $\frac{1}{4}$ in. × 2 in., in air at 70° and* 10 ft./sec.
W.B.D. = wet-bulb depression

low water-contents, velocity and wet-bulb depression have virtually no influence on the rate of evaporation and a dependence on dry-bulb temperature emerges (Fig. 5), presumably because the rate of internal diffusion depends upon it.

It is only under unusual circumstances that the rate of drying of an individual strip is of much practical interest. Strips are usually dried in layers on trays with the current of air passing tangentially across them (' over-draught '). Experiment shows that drying tends to be very uneven, and at intermediate stages a wide range of water-contents may be found among strips in different positions in the same layer. A typical result is shown in Fig. 6. The over-all effect is that the average rate of drying of such a layer is much lower than that of individual strips under the same conditions, and it is not surprising to find that for considerable periods of time the rate of drying may vary with speed and with wet-bulb depression very much as if the surface were truly ' wet.'

Fig. 7 shows the effect of the size of strip on the drying of a layer, and Fig. 8 shows the effect of wet-bulb depression and air speed. Clearly, if the air speed is not too high the rate of drying can be regarded as approximately proportional to the wet-bulb depression at quite low water-contents. This is more strikingly illustrated by Fig. 9, which shows the results of a series of tests at a variety of different dry-bulb temperatures.

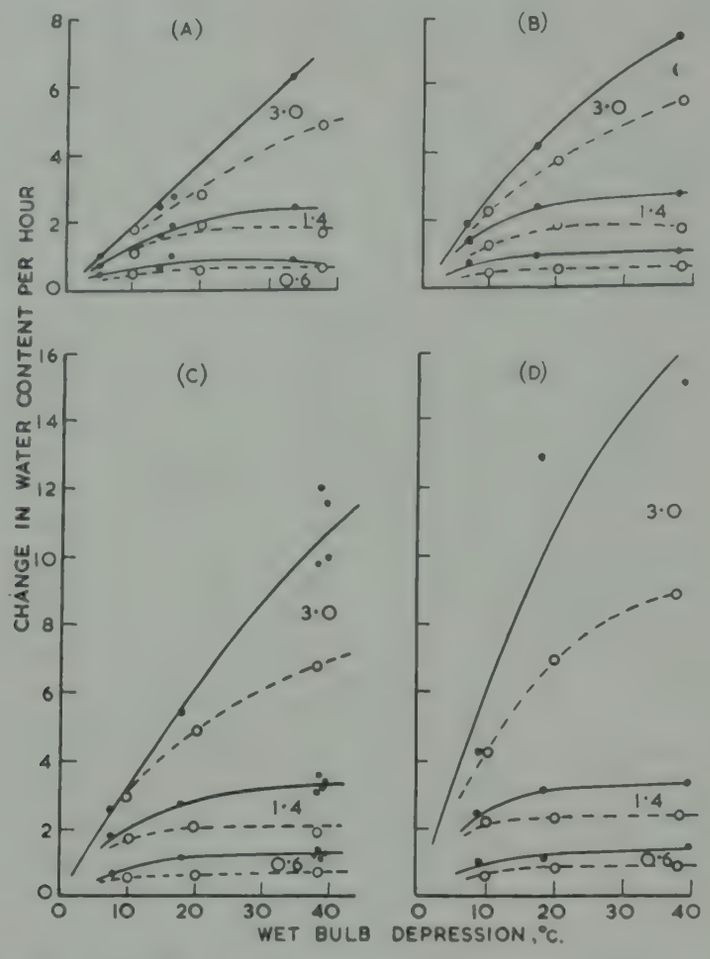

FIG. 4. *Effect of wet-bulb depression and air speed on the rate of drying of individual strips of potato at various water contents in air at 70°*

——●—— strips $\frac{3}{16}$ in. × $\frac{5}{16}$ in. × $2\frac{1}{2}$ in.
– – O – – strips $\frac{1}{4}$ in. × $\frac{1}{4}$ in. × 2 in.
A at 2 ft./sec. C at 10 ft./sec.
B at 5 ft./sec. D at 18 ft./sec.

Figures on curves are water contents

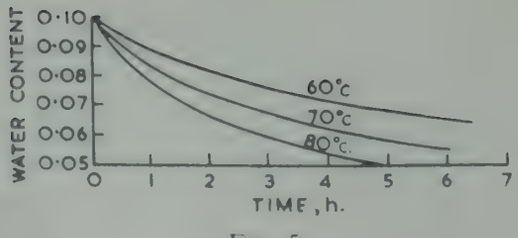

FIG. 5

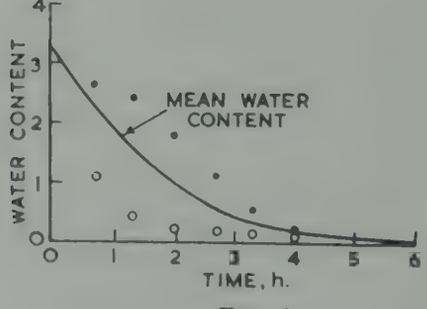

FIG. 6

FIG. 5. *Final stages of drying potato strips, $\frac{3}{16}$ in. × $\frac{5}{16}$ in., at various dry-bulb temperatures*

FIG. 6. *Variation in water-content of potato strips when dried on trays by over-draught: wettest and driest strips chosen by inspection*

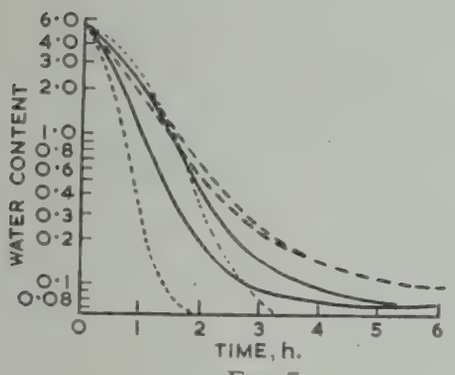

FIG. 7

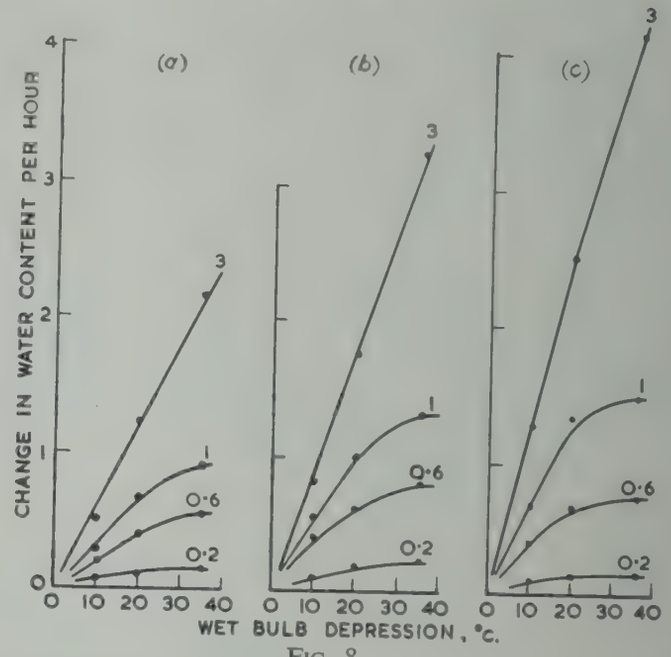

FIG. 8

FIG. 7. *Effect of size of strip on the drying of potato on trays, over-draught*

——— $\frac{1}{8}$ in. × $\frac{1}{4}$ in. ——— $\frac{3}{16}$ in. × $\frac{5}{16}$ in. ——— $\frac{1}{4}$ in. × $\frac{3}{8}$ in.

The two curves for each size relate to the upstream and downstream components of a double tray, 4 ft. × 4 ft. Dry-bulb 70°, wet-bulb depression 35°, air speed 16 ft./sec. Loading 0·24 lb. dry/ft.²

FIG. 8. *Effect of wet-bulb depression and air-speed on the rate of drying of potato strips on trays, over-draught*

Air speed: (*a*) 2 ft./sec., (*b*) 5 ft./sec., (*c*) 10 ft./sec. Dry-bulb temperature 70°, trays 10$\frac{1}{4}$ in.², strips $\frac{3}{16}$ in. × $\frac{5}{16}$ in., loading 0·35 lb. (dry)/ft.²

An important practical consideration is the effect of the thickness of layer on the tray. From many points of view thicker layers are more convenient and economical; on the other hand, very thick layers dry very slowly and quality may suffer. It is necessary to distinguish here between two rates: the rate of drying of the material, and the rate of evaporation of water from unit area of the tray. As the thickness of the layer is increased, the rate of evaporation which can be obtained under given conditions increases to maximum, since there is a limit to the extent to which the stream of air may effectively penetrate the layer (Fig. 10). The lower the mean water-content, the thicker the layer at which the maximum is reached since a layer of partially dried material is more open in structure. The rate of drying is affected differently, being a maximum for the lightest loads (which correspond approximately to individual strips) and falling off with increasing thickness (Fig. 11); at low water-contents, however, the same rate of drying is maintained until quite a thick layer is reached.

The data presented in these graphs provide, as has already been admitted, only a general indication of the effect of some of the more important factors on the rate of drying of potato. With the object of providing more direct assistance to the designer, a method of estimating drying times and rates under practical conditions has been devised; no great accuracy is claimed, but it is thought that the method will provide a reasonable basis for calculation if used with discretion and if adequate margins of safety are allowed.

The drying has been divided into two stages: from the beginning to a mean water-content of 0·1, and from 0·1 to the end. For the first period, a drying curve and the corresponding rates of drying are given in Fig. 12; they refer to a tray 2 ft. long in the direction of the air stream dried under the conditions stated with an assumed wet-bulb depression of 1 °C, and were obtained from an experimentally determined drying curve at a wet-bulb depression of 20 °C on the assumption that the rate of drying is proportional to the wet-bulb depression. It can be assumed that a tray 4 ft. long in the direction of the air flow dries about 15% slower. To convert to any given conditions, times should be divided and rates multiplied by the appropriate wet-bulb depression. To allow for different rates and air speeds, correction factors are given. The probable effect of different-sized strips can be estimated by reference to Fig. 7.

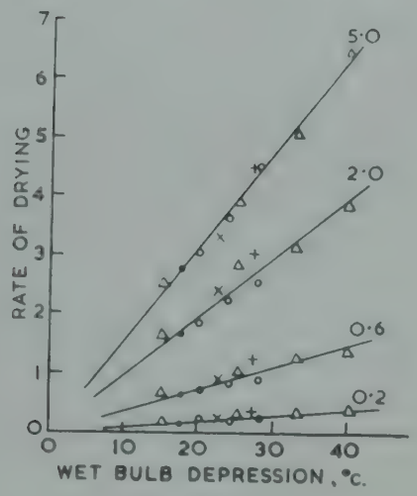

FIG. 9

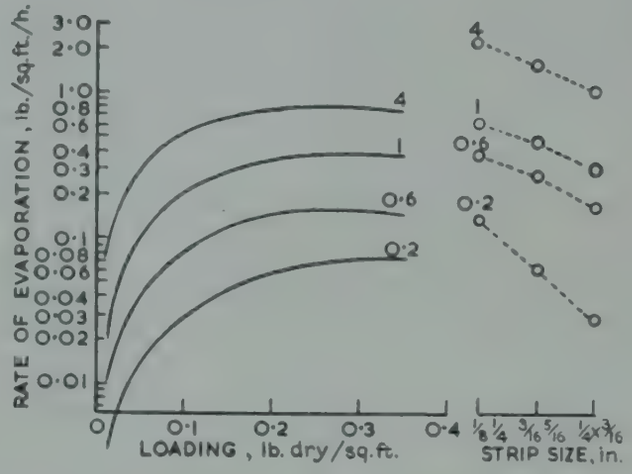

FIG. 10

FIG. 9. *Effect of dry-bulb temperature and wet-bulb depression on the rate of drying of potato strips on trays, over-draught*

Trays 10¼ in. × 10¼ in., strips $\frac{3}{16}$ in. × ¼ in., loading 0·21 lb. dry/ft.,² air speed 10 ft./sec.

Dry-bulb temperature

● 50° × 70°
○ 60° Δ 80°
\+ 90°

FIG. 10. *Effect of loading and strip size on the rate o evaporation of water per ft.² of tray during the drying of potato strips, over-draught*

——— loading curves
strips $\frac{3}{16}$ in. × $\frac{5}{16}$ in., air speed 10 ft./sec., dry-bulb 70°, wet-bulb depression 25°, trays 10¼ in.²

- - - - - - strip size curves
air speed 16 ft./sec., dry-bulb 70°, wet-bulb depression 35°, trays 4 ft. × 2 ft., loading 0·24 lb. dry/ft.²

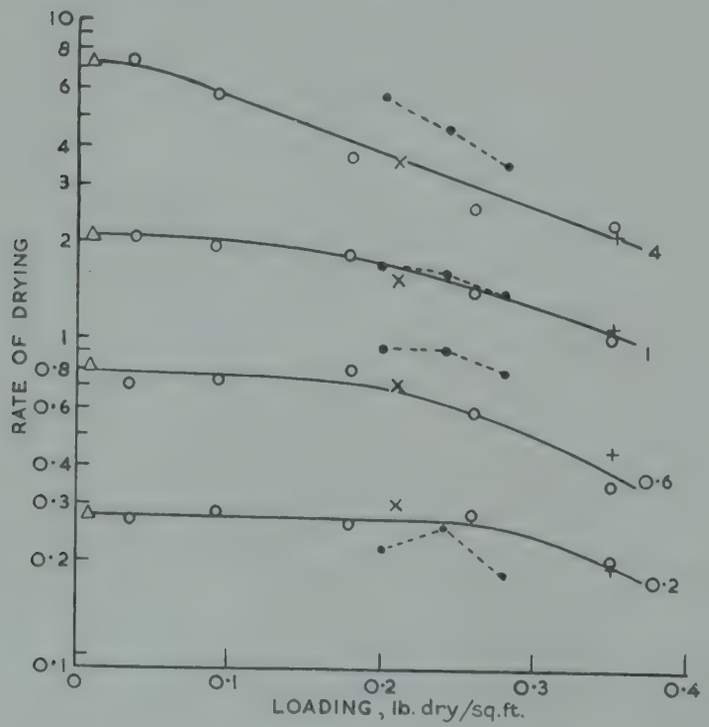

FIG. 11. *Effect of loading on the rate of drying of potato strips on trays, over-draught*

Strips $\frac{3}{16}$ in. × $\frac{5}{16}$ in. Initial water-contents: Δ 3·5, ○ 4·8, × 5·0, \+ 3·3, ● 5·2
● 4 ft. × 2 ft. tray, 35° wet-bulb depression, 12 ft./sec.
Δ individual strips, 25° wet-bulb depression 10 ft./sec.
Remainder, 10¼ in.² trays all at 70° dry-bulb, 25° wet-bulb depression, 10 ft./sec.

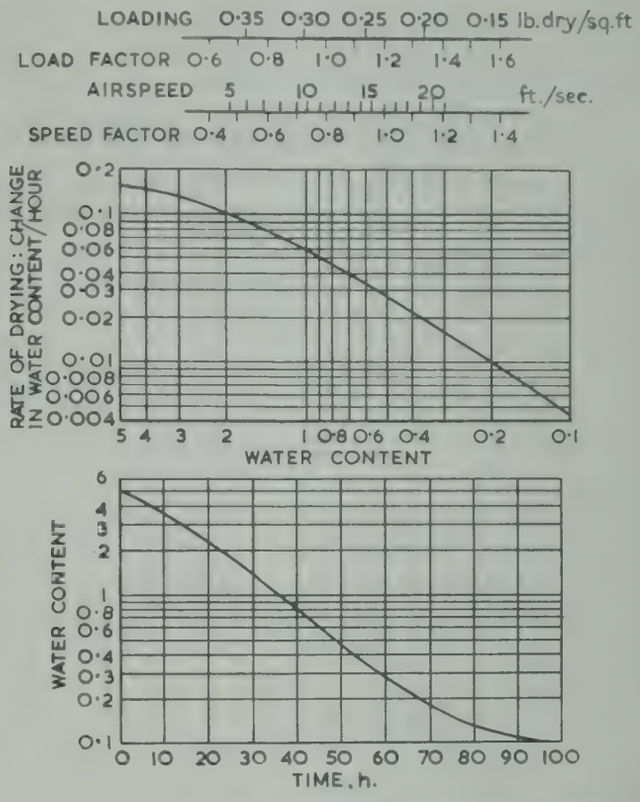

FIG. 12. *Data for calculating approximate drying times and rates for potato strips on trays, over-draught*

Appropriate to strips $\frac{3}{16}$ in. × $\frac{5}{16}$ in., loading 0·28 lb. dry/ft.,^{2} air speed 16 ft./sec. Times to be divided, and rates multiplied, by wet-bulb depression in °C. For other loadings and air-speeds, divide times and multiply rates by the factors indicated above

Drying curves for water-contents below 0·1 are given in Fig. 5. This stage of the process is virtually unaffected by velocity and loading.

A variety of other factors which cannot readily be dealt with quantitatively may arise in practice and are likely to have a considerable influence on the progress of drying. They include such departures from normality as irregular spreading and variation of air speed across the dryer. Some of these are briefly discussed in the Report referred to, which also includes a discussion of the drying of potato in a vertical current of air which passes through the layer (' through-draught ').

Table I

Comparative rates of drying, per unit wet-bulb depression, for different vegetables on trays, ' over-draught '

Water-content	Change in water-content/h./°C wet-bulb depression				
	Potato	Carrot	Beetroot	Swede	Cabbage
17	—	—	—	—	0·473
10	—	—	0·275	0·270	0·346
8	—	0·245	0·229	0·251	0·310
6	—	0·221	0·208	0·229	0·249
4	0·119	0·183	0·187	0·189	0·185
2	0·099	0·114	0·130	0·110	0·098
1	0·065	0·074	0·081	0·068	0·052
0·6	0·038	0·047	0·046	0·042	0·035
0·4	0·027	0·032	0·030	0·026	0·024
0·2	0·0124	0·0109	0·0140	0·0105	0·0118
0·1	0·0030	0·0024	0·0057	0·0024	0·0029
Loading, lb. wet/sq. ft.	1·5	1·5	1·5	1·5	1·25
Loading, lb. dry/sq. ft.	0·27	0·15	0·14	0·12	0·07
Initial rate of loss of water per sq. ft. of tray, lb./h.	0·035	0·040	0·037	0·036	0·033

Drying of other vegetables

Experiments on the rate of drying in ' over-draught ' drying, using 10½ in. square trays, were made with scalded strips of potato, carrot, beetroot and swede and with scalded shreds of cabbage. The results are given in Table I. Drying followed the same general course in all cases, but at speeds depending on the tissues. Thus swede, beetroot and carrot are very similar, but the starchy tissue of potato is dissimilar, as is cabbage, where the difference is due to its being shredded while the others are as strips.

Discussion

Mr. E. G. B. Gooding: I should like to pay tribute to this pioneer work of Mr. Ede, which has been the basis of so much of the practice of dehydration in this country during and after World War II.

Can Mr. Ede tell me whether there is, or is not, a constant-rate drying period in the early stages of dehydration of single pieces of vegetable? In commercial-scale work, using tray loads of about 1½ lb. of scalded vegetable per sq. ft., we certainly have a constant-rate period, lasting for perhaps 20 minutes under the conditions we use; I am wondering whether this is simply a result of the blanketing effect of the heavy load, or whether it is a property of the individual pieces of vegetable.

Mr. Ede: I can only refer Mr. Gooding to Fig. 3 in my paper, where it is shown that a short constant-rate drying period was apparently obtained with single strips of potato when dried comparatively slowly in air at a low wet-bulb depression, but not when the wet-bulb depression was large. It is, of course, difficult to obtain precise information about this initial stage of drying, since the weight of the strip is falling very rapidly and frequent weighings would be needed to define the drying curve closely; these frequent interruptions to the process might well invalidate the results. My impression is that a constant-rate period probably exists, but that more refined experimental techniques would be needed to detect it with precision.

DIFFUSION AND THERMODYNAMICS OF WATER IN POTATO STARCH GEL

By B. P. FISH

(*Imperial Chemical Industries, Ltd., Billingham Division*)

The dehydration process is described in terms of a diffusion coefficient which depends on the moisture content of the material. This coefficient varies over about three orders of magnitude in the range between dryness and saturation. Changes in the thermodynamic properties of water in starch gel occur as the moisture content is reduced, especially below 10% on the dry basis. The conclusion is that the slow transport of water in dry starchy material is associated with the loss of rotational freedom of the water molecules. The height of the energy barrier for the fundamental process of diffusion appears to increase as the moisture content of the material is reduced. Some practical remarks on the dehydration of gelatinous material are included.

Introduction

It is desired to eliminate some of the problems experienced in the dehydration of starchy foodstuffs, the moisture content of which must be kept low so that they can be preserved for long periods in a relatively palatable form. A representative type of material has been studied under optimum conditions where the rate of drying is controlled by the migration of water inside the material. The transport of water away from the material, and the transfer of heat to vaporize this moisture are not considered here.

The ' yard-stick ' for the rate of dehydration is a suitably defined diffusion coefficient. In macromolecular systems, where the ' intrinsic diffusivities ' of the components differ greatly, there is a wide variation of the diffusion coefficient with the concentration of the solvent or penetrant.[1] It is proposed to limit the change in moisture content in each experimental determination to a small interval, so that it becomes possible to neglect changes in the diffusion coefficient and in the volume of the material. This method follows Kokes *et al.*[2] and seems most suitable to investigate diffusion in a shrinking system. Difficulty is reported[3] in the dehydration of starchy vegetables when the moisture content is less than 10% on the dry basis. Consequently, five intervals in moisture content have been chosen between dryness and 10% moisture content and five more between 10% and 35% moisture content. These moisture contents have been defined by atmospheres of fixed relative humidity.

The most suitable method for investigating diffusion in hard brittle materials is to measure the rate of sorption and desorption of penetrant.[4] The diffusion coefficient may be deduced directly from the basic equations for diffusion in the unsteady state. Both sorption and desorption measurements must be made over each small interval of moisture content. The apparent diffusion coefficients for sorption and for desorption are calculated separately and the arithmetic mean is taken. This is a better approximation to the true mean value of the coefficient over the given interval of moisture content than either the coefficient for sorption or the coefficient for desorption alone.[5]

The moisture content of starch gel in equilibrium with the various atmospheres of controlled humidity is found in addition to the diffusion coefficients. This means that the change in Gibbs function is known for the manufacture of starch gel. The change in enthalpy can be found from the effect of temperature upon the humidity at a fixed moisture content, and also from the sensible heat of wetting. Consequently, the thermodynamics of mixing water and starch can be evaluated. Comparison of this system with benzene and rubber[6] in which the enthalpy of mixing is negligible, suggests why water is so difficult to move in dry starch.

Experimental

Materials

The most suitable shape for a sample to be used in the investigation of uni-dimensional diffusion is a thin sheet, so that diffusion is confined to the direction perpendicular to the faces of the sheet.

Starch gel.—To produce sections of starch gel, a paste of 1 part of potato starch and 5 parts of air-free distilled water is gelled in a boiling tube by heating in boiling water. (There should be no central white core.) Bubbles may be introduced if the water used is not previously boiled under reduced pressure. A satisfactory cylinder of gel is removed from the tube and left to dry partially while supported vertically to minimize deformation. Sections of about 1–3 mm. thickness are cut from this cylinder.

Thin films of dried starch are obtained when a gel which contains 1 part of starch to 8 parts of air-free distilled water is poured on to a glass microscope slide and left to dry. The thickness of the film can be adjusted from about 0·02 to 0·2 mm. by altering the composition of the paste and the thickness of the layer originally deposited. These films of starch are clear and transparent.

Potato.—Some work on dried potato has been included in the programme. It is not easy to obtain a reproducible supply of potato. Some large King Edward potatoes were obtained from the National Institute of Agricultural Botany (Cambridge) and stored at 5°C. The central medulla region of the potato is used because the cell structure is more uniform. A cylindrical core is extracted from this region and sliced on a simple microtome into sections about 1 mm. thick. These are scalded in steam for about two minutes to deactivate the enzymes which may otherwise cause a brown coloration. A sample was tested for deactivation of peroxidase by the standard peroxide–guaiacol method.[7] (Enzyme deactivation is part of the normal commercial practice in the production of dried vegetables. Scalding causes the starchy content of the cells to gel.) When left to dry, the sections shrink to give saddle-shaped pieces, but a flat disc may be produced if the section is dried with one face cemented to a glass plate by starch paste.

Measurement of the sections

The area of the face of a flat specimen is rapidly determined by projecting the outline upon sensitive paper using a photographic enlarger. The sections are compared in the photograph with a metal disc of known area. The thickness of the section is measured by a dial micrometer fitted with rounded anvils (2 mm. radius). The volume of the section is found from the weight of dry A.R.-grade benzene which is displaced. (The sorption of benzene into starch gel is not greater than 0·5% on the dry basis.) No correction has been made for thermal expansion of the sections.

Design of apparatus

Thermostatted enclosures.—Sections which weigh approximately 0·5 g. are enclosed in an atmosphere maintained at a constant humidity by dilute sulphuric acid (see [8]). About 50 ml. of acid are used in the enclosure so that the humidity does not change by more than 0·5% during the experiment. A number of these enclosures are placed in a water-bath the temperature of which is controlled to 0·1° by a mercury–toluene regulator which can operate a heater or a refrigeration unit.

A specimen is hung about 2 cm. above the surface of the acid and left to reach equilibrium. The dimensions of the sample are then measured as described above and the sample returned to its enclosure. Diffusion is followed over a small interval of moisture content by the change in weight of the specimen after it has been transferred to an enclosure at a different humidity. The specimens are removed from their enclosures and weighed on a microbalance sensitive to 10^{-5} g. To prevent any change in weight during the operation of weighing, the sections are hung inside a vessel which holds a small quantity of sulphuric acid taken from the parent enclosure.

During diffusion under these conditions there will inevitably be a slight difference in partial pressure of water vapour between the surface of the specimen and the acid. This difference depends on the efficiency of the transport process across the air-gap. In order to study diffusion of water through the solid uninfluenced by diffusion through the air, it is necessary that this difference in partial pressure is small enough to be negligible. Any errors due to the transport of water through the ambient air will be greatest at the high rates of transport which occur during the initial stages of diffusion. This will become apparent when very thin films of material are studied. An evacuated sorption balance has been used to investigate diffusion in these thin films. The sample is hung on a phosphor-bronze spring inside a cylindrical vessel controlled to within 0·1° and capable of being evacuated to 10^{-6} mm. Hg. Water vapour may be admitted to this chamber from either of two vessels which contain sulphuric acid solutions. These solutions, which have been outgassed, control the humidity in the spring chamber as before. The spring is observed by a travelling microscope and the sensitivity is sufficient to measure a change of 0·001 cm. or 10^{-5} g.

The Tensimeter

The pressure of water vapour in equilibrium with a sample of starch gel has been measured at temperatures between 10° and 40° against a column of mercury in a tensimeter. One limb of the manometer in this apparatus is evacuated, and the vapour pressure is measured directly by the stand of mercury in the other limb.[9] These levels are observed by a travelling microscope. Starch film, 0·01 cm. thick, is used so that the time required for water to diffuse out of the film when the temperature is changed shall be small. About 1·5 g. of starch film are introduced into the tensimeter so that the moisture content of the film does not change by more than 1% when the temperature is raised and more vapour is generated. The apparatus is maintained at each temperature for about 3 hours before measurements are taken, so that the vapour pressure may reach its equilibrium value. Water vapour can be pumped away to change the moisture content of the specimen. The experiments are reasonably reproducible under these conditions, and the moisture content of the gel is estimated from the vapour pressure at 25°.

Sensible heat of wetting

The calorimeter used in a 50-ml. vacuum flask controlled to ±0·1° in a water-bath. Temperature measurements are made with a Beckmann thermometer. A 1·5-g. sample of starch gel, dried for 6 months over concentrated sulphuric acid, is weighed into a thin-walled glass bulb and sealed off. The rise in temperature when this bulb is broken beneath 30 ml. of distilled water is compared with that produced by a quantity of dried recrystallized A.R. potassium chloride. Corrections are applied for the cooling of the calorimeter. The heat absorbed during the solution of potassium chloride is taken from data published by Rossini & Bichowski.[10]

Results

Effect of moisture content of starch gel

During the early stages of the diffusion process, when the moisture content at the middle of the sheet is not appreciably altered, the change in weight of the section varies as the square root of the time.

$$\frac{M_i - M_t}{M_i - M_f} = \frac{4A}{V}\left[\frac{Dt}{\pi}\right]^{\frac{1}{2}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

A numerical solution of the diffusion equation with a diffusion coefficient which varies with the concentration of the diffusing substance has been reported by Crank.[5] When the results of these calculations are plotted in the form of equation (1), the sorption and desorption curves are linear up to over 50% of the total change in weight. The gradient of the sorption curve is not necessarily equal to the gradient of the desorption curve. When the diffusion coefficient increases with concentration over the chosen interval of moisture content, the gradient of the sorption curve, and consequently the apparent diffusion coefficient for sorption, exceeds that for the desorption curve. Crank[5] could obtain no inflexion of the sorption curves near the origin when the diffusion coefficient varied with concentration in a variety of ways. Our experimental results on the sorption and desorption of water in starch may be divided into two categories according to their shape. The curves shown in the upper part of Fig. 1 are normal in shape and are characteristic of diffusion in thin or thick sections of material with a moisture content of less than 15%, but when the moisture content exceeds this figure, the behaviour of thin films of starch gel differs from the normal. This 'anomalous' behaviour is illustrated in the lower half of Fig. 1. These curves have been obtained in the evacuated sorption balance. (Considerable evidence for similar 'anomalous' behaviour is reported for a wide variety of natural and synthetic macromolecules.[12])

It is only possible to calculate the diffusion coefficient by equation (1) when the behaviour of the experimental sorption and desorption curves is normal. Apparent coefficients for sorption and desorption are measured over each interval of moisture content and the average of these is taken to represent the diffusion coefficient at the average moisture content in each interval. Experiments at low moisture content may take two or three months to complete. Diffusion in the potentially anomalous region between 15% moisture content and saturation has been investigated using sections 2 mm. thick. The extreme value of the diffusion coefficient has been measured by the uptake of water into almost saturated starch gel. This is illustrated in Table I.

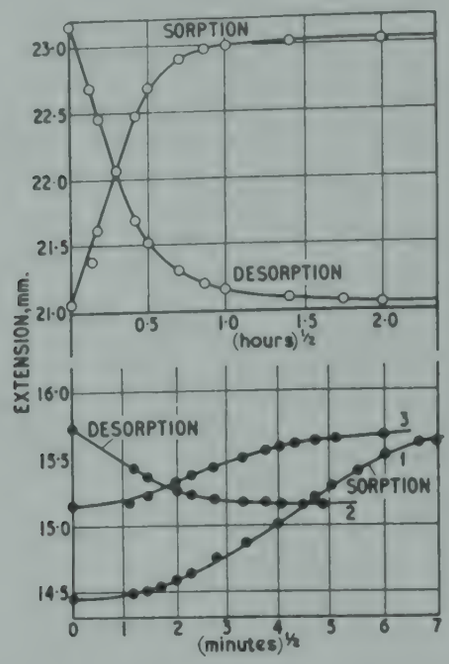

FIG. 1. *Interval sorption and desorption in starch gel*

Upper curves 14% moisture (normal)
Lower curves 18% moisture (anomalous)
1, 2, 3 show order of consecutive experiments
Temperature 25° Thickness 0·15 mm.

Table I

Uptake of liquid water into almost saturated starch gel
(thickness 2 mm.)

Moisture range, %	Average moisture content, %	Temperature, °C	Diffusion coefficient, cm.² sec.⁻¹
66–102	84	25	$2{\cdot}4 \times 10^{-7}$
67–95	81	1	$1{\cdot}3 \times 10^{-7}$
74–93	84	1	$1{\cdot}3 \times 10^{-7}$

Repeated measurements have been made on the same section and the results are reproducible to $\pm 0{\cdot}1 \times 10^{-7}$ cm.² sec.⁻¹. When different samples of starch gel are used, the reproducibility of the diffusion coefficient is somewhat greater ($\pm 0{\cdot}2 \times 10^{-7}$ cm.² sec.⁻¹.).

The diffusion coefficients obtained in the thermostatted enclosures have been tabulated in greater detail elsewhere.[11] A graphical plot of diffusion in starch gel is shown in Figs. 2 and 3. The diffusion coefficient does not begin to change until the moisture content is less than about 30%. (Moisture content is here defined as the weight of water per unit weight of dry material. It can therefore exceed 100% on the dry basis. Potatoes contain about 400% moisture on the dry basis.)

Effect of temperature

The sorption spring balance is more suitable for the study of the effect of temperature on diffusion. It is possible to make repeated measurements on a single section of starch gel over a fixed interval of moisture content. Successive sorption and desorption measurements have been made at a number of temperatures between 10 and 40 c. The average of the apparent diffusion coefficients for sorption and for desorption has been taken to be the diffusion coefficient. An Arrhenius' plot of the logarithm of this coefficient is shown in Fig. 4. An attempt has been made to randomize this order to eliminate any effect due to ageing or thermal decomposition in the gel. Each line in the figure represents a different average moisture content. The information for 80% moisture content included in Fig. 5 has been obtained from experiments in the thermostatted enclosures. Each point on this line represents the average of four determinations. (This also applies to Table I.) The diffusion coefficient may be written

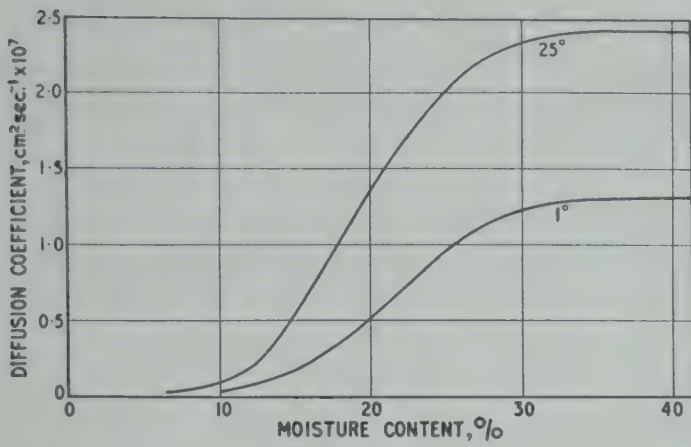

FIG. 2

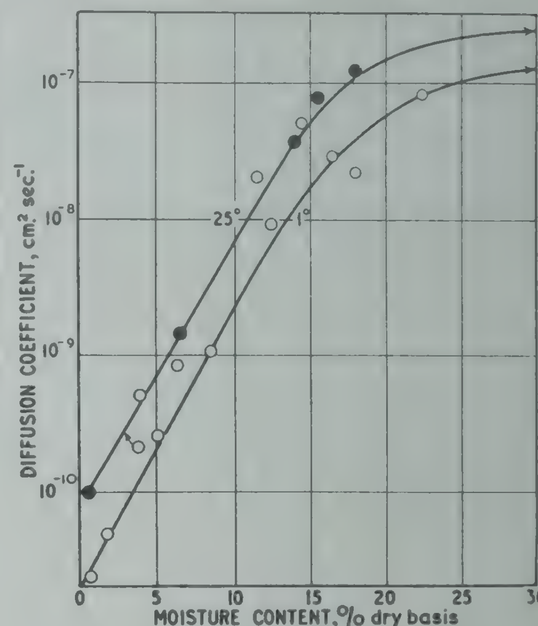

FIG. 3

FIG. 2. *Diffusion of water in starch gel*

FIG. 3. *Diffusion of water in starch gel of low moisture content*

○ enclosure ● spring

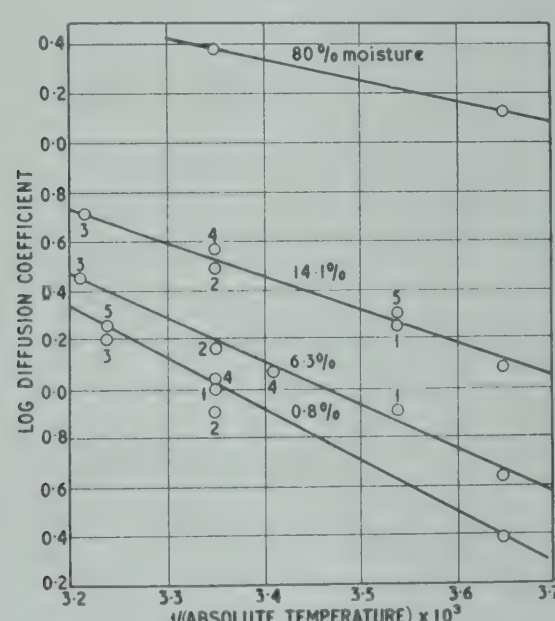

FIG. 4. *Temperature coefficient of diffusion in starch gel*

The numbers against the points indicate the order in which they were taken

in the form of equation (2) which represents activated diffusion with a minimum energy barrier (E). The information in Fig. 4 is used to calculate the coefficients in equation (2) These are recorded in Table II.

$$D = D_0 \exp(-E/RT) \quad \ldots\ldots \quad (2)$$

Table II

Activated diffusion of starch gel

Moisture content, %	D at 25°C, cm.² sec.⁻¹	D_0, cm.² sec.⁻¹	E, kcal. mole⁻¹
0·8	$1{\cdot}05 \times 10^{-10}$	$1{\cdot}2 \times 10^{-3}$	9·8
6·3	$1{\cdot}5 \times 10^{-9}$	$1{\cdot}0 \times 10^{-3}$	8·1
14·1	$3{\cdot}6 \times 10^{-8}$	$1{\cdot}2 \times 10^{-3}$	6·3
80·0	$2{\cdot}4 \times 10^{-7}$	$4{\cdot}2 \times 10^{-4}$	4·5

An error in the value of E of 0·25 kcal. mole^{-1} can affect a value of D_0 by 150%, and such an error is possible because of the scatter in the experimental data. Bearing this in mind it seems that the variation in the diffusion coefficient with moisture content may be caused more by a change in the temperature-dependent part of the coefficient.

Diffusion in scalded potato

Experiments similar to those reported above for starch gel have been made with sections of scalded potato. The coefficient for diffusion of water in scalded potato is shown as a function of moisture content in Fig. 6. The trend of these curves is similar to those for starch gel.

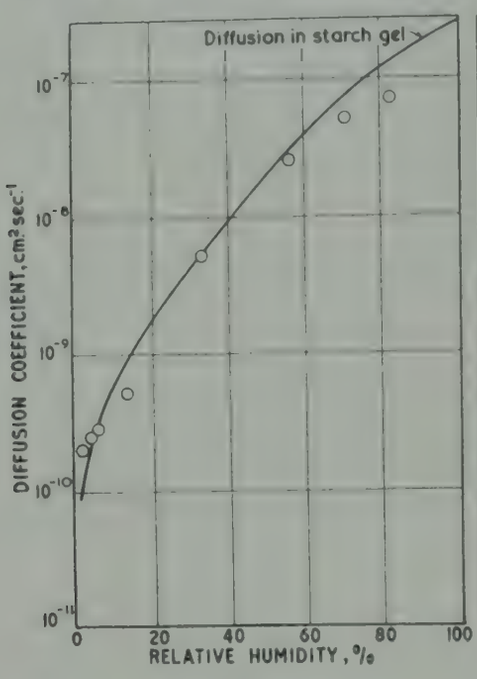

FIG. 5

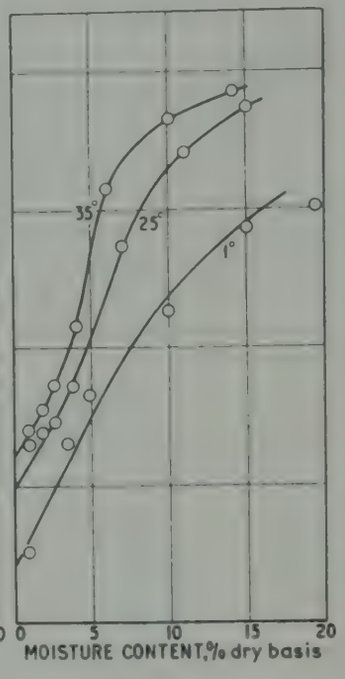

FIG. 6

FIG. 5. *Diffusion of water in scalded potato at 25° and in starch gel*
O values for sections of potato

FIG. 6. *Diffusion of water in scalded potato*

At the same ambient relative humidity, the moisture content in a sample of scalded potato will be less than that in pure starch gel because of the other components in potato. This may account for the sigmoid shape of the curves in Fig. 7. The diffusion coefficient may be plotted against the ambient humidity. The continuous line in Fig. 5 refers to diffusion in pure starch gel, and the circles refer to experiments with scalded potato. The fit implies that at similar ambient humidities the moisture content in the starchy part of the potato will not differ greatly from that in a sample of starch gel. This also implies that the diffusion of water in scalded potato is controlled by the migration of water through the starchy part of the material.

Thermodynamics of mixing water and starch

Change in the Gibbs function.—The change in the partial Gibbs function ($\Delta\bar{g}_1$) is defined as the increase in the Gibbs function for the system when 1 g. of water is transferred isothermally from a bulk of liquid water to an infinite quantity of starch gel at a definite moisture content. This change is obtained from the vapour pressure of water over a gel at any given moisture content, or in other words, the equilibrium moisture content at various humidities (equation 3).

$$\Delta\bar{g}_1 = (\bar{g}_1^m - g_1^0) = \frac{RT}{M} \ln \frac{p_1^m}{p_1^0} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

The change in the partial Gibbs function for the starch component of the gel ($\Delta\bar{g}_2$) is defined similarly to that for the aqueous component ($\Delta\bar{g}_1$). These partial functions are related by the Gibbs–Duhem equation (4) written in terms of the weight fraction (W) of water.

$$W\mathrm{d}(\Delta\bar{g}_1) + (1 - W)\,\mathrm{d}(\Delta\bar{g}_2) = 0 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4)$$

$$\text{or} \quad \Delta\bar{g}_2 = \frac{-RT}{M} \int \frac{W}{1-W} \cdot \frac{1}{a} \cdot \mathrm{d}a \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (5)$$

where $a = p_1^{\mathrm{m}}/p_1^{\circ}$, or the relative humidity.

Equation (5) enables the change in the partial Gibbs function for the starch component to be calculated from the ' water relations.'

The change in the Gibbs function ($\Delta\bar{g}^{\mathrm{m}}$) when 1 g. of gel is manufactured from starch and liquid water is given by

$$\Delta g^{\mathrm{m}} = W\Delta\bar{g}_1 + (1 - W)\,\Delta\bar{g}_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (6)$$

Ambiguity due to hysteresis occurs at high relative humidities where the same water vapour pressure is produced by gels of different moisture contents. The changes in the Gibbs function are small at high relative humidities, and so the effect of hysteresis is relatively unimportant. All the available data on the ' water relations ' of starch gel, including the work of Farrow & Swan,[13] have been collected into the left-hand portion of Fig. 7. The smoothed curve has been used to compute the change in the Gibbs function (Δg^{m}) in Fig. 8.

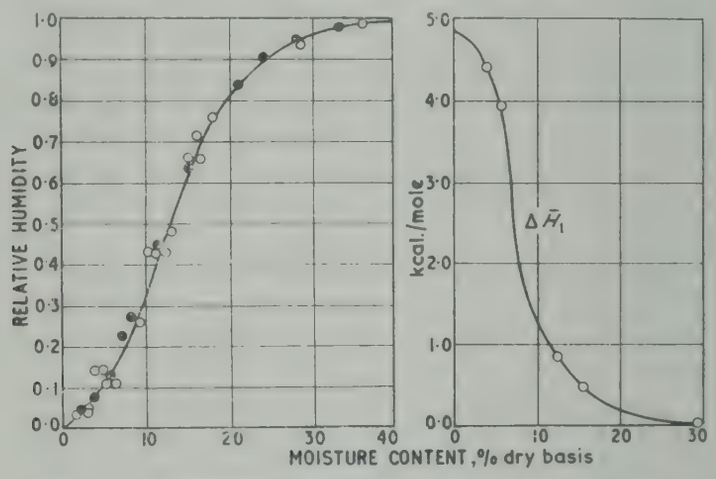

FIG. 7. *Experimental data for thermodynamic functions in starch gel*

Water relations of starch gel at 25°
● Farrow & Swan

Partial molar enthalpy of dilution in starch gel
○ This work

Change in enthalpy.—The change in the partial enthalpy ($\Delta\bar{h}_1$) for the aqueous component is defined in the same way as $\Delta\bar{g}_1$ above, except for the substitution of the concept of enthalpy. Under reversible conditions the partial enthalpy change per g. of added water is given by equation (7)

$$\Delta\bar{h}_1 = (\bar{h}_1^m - h_1^o) = -\frac{RT^2}{M} \cdot \frac{\partial}{\partial T}\left[\ln \frac{p_1^{\mathrm{m}}}{p_1^0}\right]_{P,W} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (7)$$

where the superscripts (m) and (o) refer to the mixture and to the pure component respectively. The Gibbs–Duhem relation can again be applied to give the change in the partial enthalpy for the starch component ($\Delta\bar{h}_2$) in the mixture thus:

$$\Delta\bar{h}_2 = -\int \frac{W}{1-W}\,\mathrm{d}(\Delta\bar{h}_1) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (8)$$

The tensimeter has been employed to measure the effect of temperature on the vapour pressure over starch gel. The results are used to calculate the partial enthalpy change for water ($\Delta\bar{h}_1$) by equation (7). The range of temperature over which measurements have been made is 5° to 40° C. The right-hand half of Fig. 7 shows the partial enthalpy change per mole of water ($\Delta\bar{h}_1$ or $M\Delta\bar{h}_1$).

The partial enthalpy change for the starch component ($\Delta\bar{h}_2$) has been calculated from the smoothed curve in the right-hand part of Fig. 7. At high moisture content this tends to the value 23·6 cal. g.$^{-1}$ Starch of very high moisture content is thermodynamically similar to pure water. Consequently the limiting value of ($\Delta\bar{h}_2$) is similar to the sensible heat of wetting

for 1 g. of dry starch. Several determinations of the heat of complete wetting of dried starch gel by the method outlined above give the value $-24{\cdot}6 \pm 0{\cdot}3$ cal. g.$^{-1}$ If it is assumed that $(\Delta\bar{h}_2)$ must approach this value, a correction can be applied to $(\Delta\bar{h}_1)$ by the Gibbs–Duhem equation again. The enthalpy change when 1g. of gel is manufactured from starch and liquid water is given by equation (9) and is plotted in Fig. 8.

$$\Delta h^{\mathrm{m}} = W\Delta\bar{h}_1 + (1 - W)\,\Delta\bar{h}_2 \quad \ldots\ldots (9)$$

Change in entropy.—Partial entropy changes $\Delta\bar{s}_1$ and $\Delta\bar{s}_2$ are defined per g. of each component as before, and these are again related by the Gibbs–Duhem relation. The change in entropy when 1 g. of starch gel is manufactured from the components is given by

$$T\Delta s^{\mathrm{m}} = \Delta h^{\mathrm{m}} - \Delta g^{\mathrm{m}} \quad \ldots\ldots (10)$$

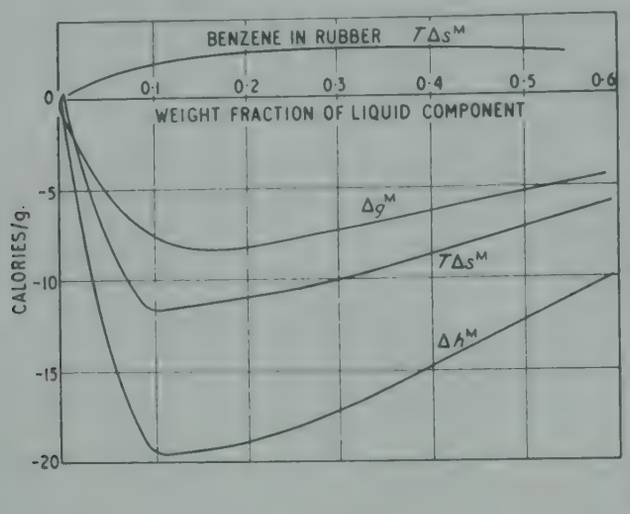

FIG. 8

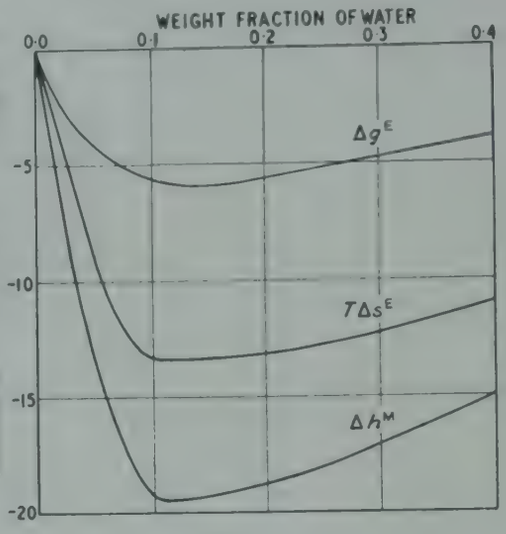

FIG. 9

FIG. 8. *Thermodynamic functions for making* 1 *g. of starch gel at constant pressure* (1 *atmosphere*) *and* 298°K
(Comparison with an athermal macromolecular solution)

FIG. 9. *Excess thermodynamic functions for making* 1 *g. of starch gel at constant pressure* (1 *atmosphere*) *and* 298°K

The thermodynamic functions for mixing one g. of starch gel are plotted together in Fig. 8. The partial thermodynamic functions can be obtained from this figure if the tangent is constructed to the curves at the required moisture content. (The data have been tabulated in a previous report of this work.[11]) When water is added to an infinite quantity of dry starch the entropy change must be infinite. The curve for (Δs^{m}) therefore takes a maximum near dryness and the curves for (Δg^{m}) and (Δh^{m}) intersect just beyond this maximum.

The position of the curves in Fig. 8 cannot be guaranteed to better than half a calorie. The departure from reversible conditions in the tensimeter cannot be so great, however, in view of the agreement between the integrated value of $(\Delta\bar{h}_1)$ and the sensible heat of wetting.

Discussion

Departure from ideal behaviour in macromolecular solutions

The macromolecular solution of rubber in benzene approaches 'ideal' conditions in that the enthalpy change on mixing is very small, and the entropy change on mixing controls the change in the Gibbs function. It is possible to follow the usual treatment in simple binary mixtures[14] and divide the entropy change in the manufacture of starch gel into two parts.

$$\Delta s = \Delta s\,(\text{ideal}) + \Delta s\,(\text{excess}) \quad \ldots\ldots (11)$$

It is suggested that the ideal entropy change can be taken from the experimental results of Gee & Treloar[6] on the athermal solution of rubber in benzene. The 'excess' entropy in the manufacture of 1 g. of starch gel is then calculated as in Table III. Because the partial densities of the components are similar in each of the two systems, comparison may be made at equal weight fractions.[15]

Table III

Weight fraction of solvent	Rubber in benzene,[6] cal./g.	Starch and water (Fig. 8) $T\Delta s$, cal./g.	Excess entropy, cal./g.
0·02	+0·61	− 3·1	− 3·7
0·04	+0·99	− 6·2	− 7·2
0·06	+1·30	− 8·9	−10·1
0·08	+1·55	−10·8	−12·4
0·10	+1·79	−11·6	−13·4
0·20	+2·46	−10·9	−13·1
0·30	+2·67	− 9·6	−12·3
0·40	+2·66	− 8·4	−11·1

The other ' excess ' thermodynamic functions have been calculated in the same way as in Table III, and are plotted in Fig. 9. The solution of water in starch differs from that of benzene in rubber in two ways. When starch and water are mixed isothermally there is a large decrease in the entropy and evolution of heat. The curves in Fig. 9 take a minimum near the weight fraction 0·1, at which the over-all composition is one water molecule (mol. wt. 18) to one glucose residue (mol. wt. 162). This ties up with the *X*-ray structure of the starch crystallite. Although the observation is controversial (cf. Rundle[16]), Kreger supposes that there is one water molecule to each glucose residue in the crystalline fraction of starch.[17] The partial ' excess ' functions for 1 mole of a mixture of water molecules and starch residues are recorded in Table IV.

Table IV

Partial ' excess ' functions for 1 mole of ($H_2O + C_6H_{10}O_5$ residues)

Moisture content, %	Dilution $\Delta\bar{s}^{E}_1$ per H_2O entropy units mole	Solution $\Delta\bar{s}^{E}_2$ per $C_6H_{10}O_5$, entropy units mole	Partial enthalpy, $\Delta\bar{H}_1$, kcal./mole
0·0	−10·2	small	−4·9
2·1	−10·8	,,	−4·7
4·2	−10·8	,,	−4·4
8·7	− 5·8	−4·1	−1·8
17·5	− 0·5	−7·6	−0·27
33·3	− 0·2	−8·6	−0·01
54·0	small	−9·0	small
100·0	,,	−9·8	,,

Interaction between water and starch

The figures in Table IV mean that when 1 g.-mole of water is transferred isothermally from a bulk of liquid water to an infinite quantity of dry starch, the change in entropy is about 10 entropy units (e.u.) less than in a mixture in which the components exert no interaction. The same result is obtained when 1 g.-mole of glucose residue is added to an infinite quantity of fully swollen starch gel. The molar entropy of rotation of water molecules is 10·48 e.u.[18] If the interaction between water and dry starch involves restriction of the rotation of water molecules, the large value of the ' excess ' entropy may be reconciled. (The molar entropy of fusion of water is only 5·26 e.u.)

The ' excess ' enthalpy change of about 5 kcal./mole due to the interaction of water and dry starch may be associated with the formation of an extra hydrogen bond compared with liquid water. This may account for the relatively slow migration of water in dry starch.

' Driving force ' behind diffusion

All the diffusion coefficients discussed in the previous sections (e.g., equation 1) have been defined according to Fick's Law, in which the ' driving force ' for diffusion is the concentration gradient. An alternative approach, suggested probably by Willard Gibbs, is that the ' driving force ' is the gradient in the chemical potential of the diffusing species, which is the partial molar Gibbs free energy (compare equation 3). In solvent extraction, for instance, diffusion can take place in the direction of lower activity and opposite to the direction of lower concentration. This suggests that the approach by way of chemical potential is the more fundamental. Equation (3) suggests that the ' driving force ' for diffusion is the gradient in the pressure of water vapour,

but this implies that the diffusing species is in equilibrium with the substrate during the whole course of migration, an assumption which is difficult to justify.[19] The coefficient in Fick's Law can be associated with random movements of the particles. Transport in one direction is then favoured because the probability of transfer depends on the concentration. The coefficient based on chemical potential is associated with a flux of material under an applied force which is the derivative of the potential energy in the direction of transfer. The coefficients are related in equation (12) in which the activity coefficient at moisture content m is (f_1).

$$\frac{D_{\text{Fick}}}{D_{\text{potential}}} = 1 - \frac{\partial \log f_1}{\partial \log m} = \frac{\partial \log p_1/p_1^0}{\partial \log m} \quad \ldots\ldots (12)$$

The derivative of the curve shown in Fig. 7 indicates that this ratio is approximately 1·5 at moisture contents between 2 and 18%. At higher moisture contents the ratio diminishes to reach approximately 0·02 near saturation. The coefficients are equal when Henry's Law is obeyed.

Activated diffusion in starch of low moisture content

In starch of low moisture content the observed diffusion coefficient may be related to the coefficient for the migration of water relative to the starch fibrils, because these are relatively less able to move. *X*-ray evidence[17] suggests that successive water molecules in the starch crystallite are separated by a distance (λ) of 3·5 Å. If there is a periodic energy barrier of height U along the starch fibrils, the probability of transfer will be given by $\exp(-U/RT)$ in the simple example where two quadratic terms contribute to the activation process. If the crystallites are randomly oriented, the probability that the motion of the water molecule will lie in the direction of diffusion will be

$$P = \tfrac{1}{4}\pi \int_0^{\pi/2} 2\pi \sin\theta \cos\theta \, d\theta = \tfrac{1}{4}.$$

The diffusion coefficient is then given by equation (13), and the coefficients of the Arrhenius equation (Table II) by equation (14).

$$D_0 = \frac{\lambda^2 kT}{4h} \exp(-U/RT) \quad \ldots\ldots (13)$$

$$D_0 = 2{\cdot}72 \frac{\lambda^2 kT}{4h}, \qquad E = U + RT \quad \ldots\ldots (14)$$

At 25° the theoretical estimate of D_0 by equation (14) is $5{\cdot}2 \times 10^{-3}$ cm.^{2} sec.$^{-1}$ The observed values in Table II are somewhat smaller than this. If the activation process is associated with more than two degrees of freedom, the calculated value of D_0 will be greater, as in elastomeric systems where the large 'region of disorder' during activation gives D_0 values of 10^{-1} to 10 cm.^{2} sec.$^{-1}$

Diffusion at intermediate moisture content

Changes in the diffusion coefficient are controlled largely by the apparent energy of activation. There is a similar trend with moisture content in both the partial molar enthalpy of dilution (ΔH_1) and the observed value of the activation energy, which is shown in Table V.

Table V

Energy of activation and of dilution

Moisture content, %	Partial molar enthalpy of dilution ΔH_1, kcal./mole	Observed energy of activation, kcal./mole	$-\Delta H_1 + 4{\cdot}6$, kcal./mole
1·0	−4·9	9·8	9·5
6·3	−3·4	8·1	8·0
14·1	−0·67	6·3	5·3
80·0	0·0	4·5	4·6

In Table V, the figure 4·6 kcal./mole is a recent value reported[20, 21] for the energy of activation of self-diffusion in water.

When the moisture content exceeds about 15%, the interaction between water and starch ceases to affect the diffusion process. The activation energy for diffusion in saturated gel is similar to that for self diffusion in water. One may apply the correction for deviation from Henry's Law (equation 12) to the coefficient for diffusion in saturated gel (2×10^{-7} cm.^{2} sec.$^{-1}$ at 25°) measured according to Fick's Law. The coefficient for the flow of water in saturated gel under the action of the force derived from the chemical potential is 10^{-5} cm.^{2} sec.$^{-1}$ at 25°C. Is it significant that this is of the order generally obtained for self-diffusion in water?

Practical considerations

Uni-axial diffusion in a system which shrinks in three dimensions

When diffusion is accompanied by a change in volume it is necessary to define a plane of reference so that there is no transfer of dry material from one side to the other during diffusion.[22] The usual diffusion equations may then be applied. Such a plane of reference will move with the boundaries of the section of material. The effect of the change in convention is to define displacement so that equal increments cut off equal weights of dry material instead of equal lengths of gel. In the special case where equal weights of dry material in the section occupy the same volume when the section is completely dry, a ' pseudo ' diffusion coefficient can be defined with respect to the dimensions of the dry section. This ' pseudo ' coefficient will contain the second power of the displacement, and if the system shrinks isotropically in three dimensions the ' pseudo ' coefficient will be related to the ' proper ' diffusion coefficient previously measured (Figs. 2–6) by equation (15).

$$\frac{\text{' pseudo ' coefficient}}{\text{' proper ' diffusion coefficient}} = \left(\frac{\text{Volume of dry section}}{\text{actual vol. of section}}\right)^{\frac{2}{3}} \quad \ldots\ldots\ldots\ldots\ldots\ldots (15)$$

(In the original paper by Hartley[22] the area of the section remains constant, while the shrinkage takes place only along the direction of diffusion. Under these conditions the 2/3 power in this equation is replaced by the square.)

Measurements have been made on the specific volume of starch gel at various humidities by the displacement of benzene. The diffusion coefficient shown in Fig. 2 has been adjusted by equation (13) to give the ' pseudo ' coefficient illustrated in Fig. 10. The ' pseudo ' coefficient tends to vanish in dilute gels because of the small proportion of dry matter in such material. The ' pseudo ' coefficient can be integrated to give the effective value for diffusion from an initial moisture content (m_i) to a final moisture content (m_f).

$$D_e = \frac{\int_0^{m_i} D_{\text{pseudo}}\, dc \;-\; \int_0^{m_f} D_{\text{pseudo}}\, dc}{m_i - m_f} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (16)$$

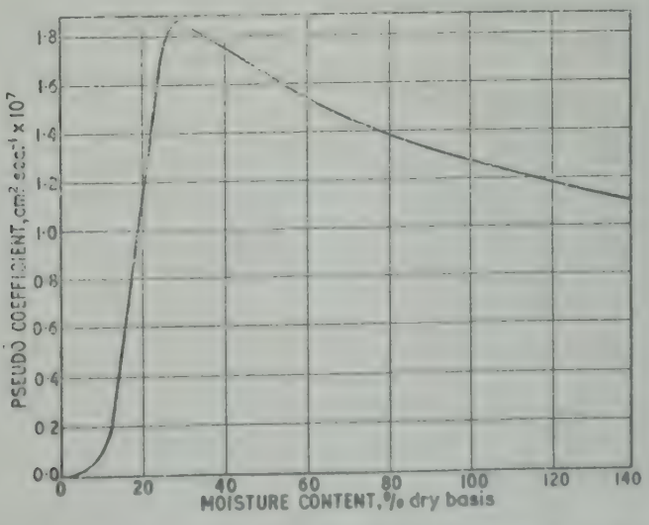

FIG. 10. *Pseudo coefficient in starch gel referred to dry dimensions 25°*

For instance, the effective value of the ' pseudo ' coefficient for diffusion between dryness and 140% moisture content can be obtained by application of the integral (equation 16) to Fig. 10. The ' pseudo ' coefficient is thus estimated to be $1{\cdot}27 \times 10^{-7}$ cm.^{2} sec.$^{-1}$ (referred to the dry dimensions). This is consistent with the experimental value $1{\cdot}23 \times 10^{-7}$ cm.^{2} sec.$^{-1}$ (referred to the dry dimensions) which is the average ' pseudo ' coefficient (25°) measured for sorption and desorption of water in starch gel over the interval of moisture content between dryness and 146%.

Drying over large intervals of moisture content

The concept of the ' pseudo ' coefficient is useful to make simple calculations. A number of effective values of the ' pseudo ' coefficient has been tabulated in Table VI, which can be used in an equation such as (17).

$$\frac{M_t - M_f}{M_i - M_f} = \frac{8}{\pi^2} \sum_{v=0}^{v=\infty} \frac{1}{(2v+1)^2} \exp\left\{-(2v+1)^2 \frac{\pi^2 Dt}{l^2}\right\} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (17)$$

Suppose that a section of starch gel initially at 140% moisture content is placed in a bone-dry atmosphere. When dry, the thickness of the section will be 0·1 cm. Calculations indicate that the section will reach an over-all moisture content of 5% after about 4 hours. This section will have a rather moist centre, but on storage the moisture content will become uniform. If the section is dried initially to a *uniform* moisture content of 10%, a section 0·1 cm. thick with 5% moisture content will be produced in 25 hours. This is because the gradient in the moisture content is small, and the effective ' pseudo ' coefficient is also small compared with more saturated material. It is therefore inadvisable to dry starchy material in successive stages.

Table VI

Drying starch gel at 50°

Initial moisture content, %	Ultimate moisture content, %	Effective ' pseudo ' coefficient, cm.^{2} sec.$^{-1} \times 10^{-7}$
140	0	2·19
30	0	1·23
10	0	0·05
140	30	2·45
30	10	1·8

Acceleration of drying

The difficulty observed in the dehydration of starchy vegetable material is due to the slow migration of water in the sections. More rapid drying can be obtained by the use of thin sections and high temperatures. If it is possible to introduce porosity into thick sections this will accelerate drying, especially under reduced pressure. Such treatment may, however, be deleterious to the texture.

Appendix

Anomalous behaviour in thin sections

Anomalous sorption curves observed in thin films of starch gel at moisture contents greater than 15% have already been described. This behaviour cannot be explained by diffusion with a coefficient which depends on the concentration of diffusing substance.[12] Crank has proposed a first-order relaxation process for temporal changes in the diffusion coefficient,[12]

$$\left(\frac{\partial D}{\partial t}\right)_c = \frac{D_c - D}{\tau} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Here the value of the diffusion coefficient (D) depends not only on the concentration (c) but also on the time (t) for which it is maintained. The equilibrium value, D_c, corresponds to the value of the coefficient when the concentration is maintained for a long time. The relaxation time for the process is τ. It may be possible to observe these temporal changes in diffusion experiments where the coefficient does not change much because the variation in moisture content is restricted.

Equation (1) above is integrated and the diffusion coefficient ($D_{c,t}$) is substituted into the diffusion equation in one dimension.[11] The change in weight of a section is then given by equation (2).

$$D_{c,t} = D_{c,\infty} [1 - a \exp(-t/\tau)]$$

$$\frac{M_t - M_f}{M_i - M_f} = \frac{8}{\pi^2} \sum_{\nu=0}^{\nu=\infty} \frac{1}{(2\nu + 1)^2} \exp \left\{ (2\pi + 1)^2 \frac{\pi^2 D}{l^2} \left[a\tau - a\tau \exp(-t/\tau) - t \right] \right\} \quad (2)$$

This reduces to the simple equation (3) during the later stages of diffusion.

$$\ln M = D(a\tau - t) \quad (3)$$

where $M = \frac{\pi^2}{8} \frac{M_t - M_f}{M_i - M_f}$, $D = \frac{\pi^2 D}{l^2}$, $0 \leqslant a < 1$ for sorption, $0 \geqslant a > \infty$ for desorption

The experimental data can be plotted according to equation (3). At moisture contents below 15% when the starch gel is brittle, the relaxation time, τ, is similar in magnitude to the time occupied by the diffusion process, represented by D^{-1}.

Above 15% moisture content, the gel ceases to be brittle and becomes pliable (but not rubbery). The relaxation time calculated by equation (3) is now unrelated to the time occupied by the diffusion process. The relaxation time can be bracketed between 200 and 300 sec. under these conditions. This is similar to the time for stress relaxation in starch gel, which has been found directly to be approximately 500 sec. at 15% moisture content. 'Ungumming' or re-orientation of the gel structure may occur in pliable starch gel under the stresses imposed by movement of the diffusing substance in the material. At high moisture content this proceeds spontaneously at a rate independent of the diffusion. In thick sections, diffusion is the slower process, and sorption follows a normal course. In thin films the ungumming process predominates during the initial stages of sorption, and sorption appears to be anomalous.

Nomenclature

A = Area of one face of a sheet
D = Diffusion coefficient
M = Weight of section
V = Volume of a section
W = Weight fraction of a component
a = Change in diffusion coefficient $(D_f - D_i)/D_f$
g = Gibbs's function per g.
h = Enthalpy per g.
l = Thickness of a section
s = Entropy per g.
ν = An integer
τ = Relaxation frequency

Superscripts
m = Mixture
o = Pure component
— = Partial thermodynamic function
E = Excess over ideal mixing

Subscripts
1 = Liquid volatile component
2 = Solid non-volatile component
c = At a given concentration
f = Final value
i = Initial value
t = At a given time
∞ = A steady value

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Discussion

Prof. D. D. Eley: Dr. Fish has emphasized the importance of loss of rotation in deciding the entropy loss of water molecules adsorbing on starch. In addition, the radial vibration of the water molecules against the polar group and the lateral translation of the water molecules need to be considered. It might be worth extending the type of calculation made some years ago for ions in water,[1] to the adsorption of water molecules on to the polar groups present in starch and in proteins.

Reference

[1] Eley, D. D., & Evans, M. G., *Trans. Faraday Soc.*, 1938, **34**, 1093

Dr. Fish: The entropy of mixing water and starch may result from a change in entropy of the 'solvent' water relative to the standard state of liquid water or to a change in the entropy of the 'solute' starch. I have naively supposed that the observed entropy change is due entirely to changes in the water molecules. I am indebted to Prof. Eley for bringing his paper to my notice. (The observed entropy of solution of ions has been shown to depend largely on the change in entropy in the co-ordinate shell of water molecules around the dissolved ion.) This supports my notion that the entropy change in the starch water system is more associated with the changes which take place in the water. However, Prof. Eley has been able to divide the entropy change in the water into the difference in vibrational entropy, translational entropy and radial vibrational entropy of a water/water molecule system and a water/ion system. Because the change in translational entropy of water molecules on solutions of an ion is large, it may follow that the entropy I have observed on mixing water and starch is due both to *changes* of rotational or vibrational entropy, and also to *changes* in translational entropy and not to a *complete restriction* of rotational entropy. Compared with the solution of ions, it would, I think, be more difficult to make precise calculations for these different entropy changes on mixing starch and water.

Mr. J. C. Forrest: Experiments were carried out at the Experimental Factory in an effort to accelerate the bin-drying stage of potato strips. It was shown that the use of heated desiccated air as compared with heated atmospheric air had very little effect on the drying rate. In the course of this work, however, the effect of an interrupted drying cycle was studied by taking potato strips ($\frac{3}{16}$ in. by $\frac{5}{16}$ in.) from the main dryers when they had reached a mean moisture content of 10% approx. Some of this material was transferred directly to the finishing bin while the remainder was stored in a sealed container, in one case for three days and the rest for six days prior to further drying. The final moisture contents were in the region of 5% and the indication was that the driest product was that which had been stored between stages for the greatest length of time.

I understand that in the U.S.A. the manufacturers of noodles package their product when the 10% moisture level is reached and transport it to the soup manufacturers for finishing drying since this second stage can be completed in a shorter time after what they call the 'sweating' period.

This does not appear to be in agreement with Dr. Fish's findings as reported on p. 154, as the drying of potato strips in successive stages does seem to reduce the time in the dryer to reach a given moisture content.

Dr. Fish: Ambient air in a dryer at 145°F dry-bulb temperature and 80°F wet-bulb temperature has a percentage humidity of 5%. The ultimate moisture content in equilibrium with this is approximately 2% on the dry basis. The ultimate moisture content with specially dried air may be 1% or less. Other things being equal, at the time when the average moisture content of a sample dried in hot air is 8%, the expected value with specially dried air will still be about 7%. The advantage of using specially dried air will not become apparent until the moisture content is reduced to about 3%.

The results of drying in successive stages are most interesting. If the drying process is stopped before equilibrium has been reached and the material is stored in a sealed container, some water will move from the centre to the faces of the sections because the centre has been left relatively more moist. Subsequent drying will then be accomplished in a shorter time than if the drying process were continued originally, *provided that* the diffusion coefficient for transport of water in the section has not been modified. My observations on starch have led me to believe that the diffusion coefficient will be modified after storage. In your observations on potatoes and noodles this modification apparently does not take place.

The concept 'sweating period' tempts me to wonder whether isothermal distillation takes place on storage of these materials with the consequent loss of water from the samples. Are there beads of water on the walls of the containers under these conditions?

In reply to a questioner who finds that he can dry $\frac{3}{16}$ in. potato strips equilibrated at 10% moisture content in 6 h. to reach 5% moisture content, *Dr. Fish* said that these experimental conditions are identical with those in his calculation with the exception that the dry-bulb temperature (140°F) is 10°C higher than in his Table VI. Nevertheless, it is hard to reconcile these observations and his calculations. Obviously more work is required before any reliable estimate of drying time can be predicted from the properties of starch gel.

Replying to a question on the rôle of transfer through the gas phase, *Dr. Fish* observed that effect of transport through the ambient atmosphere becomes more pronounced when the resistance to transport in the solid is low, i.e. when the diffusion coefficient in the solid is high. (In two consecutive processes the one with the higher resistance will control the over-all rate.) In thin films, the major part of drying takes place at a high rate of transfer of water vapour away from the material. Under these conditions the transport of water vapour in the ambient atmosphere can affect the over-all rate of drying. As Prof. Leniger has explained, the result is the establishment of a small difference in partial pressure of water vapour between the surface of the material and some remote point in the air stream. In a thick section, the rate of drying progressively decreases, and so this partial-pressure difference must also diminish. *Dr. Fish* believes that, because of the shape of his drying curves, his technique has so accelerated transport of water away from the sections that he could neglect these effects.

EXPERIMENTAL CONTRIBUTION TO THE EVAPORATION OF WHEAT DURING ARTIFICIAL DRYING

By PROFESSOR Ir. J. J. I. SPRENGER

(*Wageningen, Holland*)

As a result of many experiments made at Wageningen on the drying of grain, it has been shown that the drying curve (rate of evaporation *vs.* moisture content on dry basis) consists of three straight line segments, representing different phases of the drying process. It is now shown that the second period is the main phase: a rate law for this phase is proposed.

The first period is a modification of the second one and is caused by heating of the grain. During this period the evaporation rate is higher than in the second one.

The third period starts at about 17·5% relative humidity. The different behaviour during this period is attributed to a different physical law of evaporation.

A complicated final drying stage follows this third period, but as it is never reached in drying practice it is of academic interest only and is not considered here.

Introduction

Grain and seeds can only be stored in a good condition if the moisture content does not exceed a certain limit, which is usually between 14 and 17%, depending on storage conditions. If the moisture content at harvest does not greatly exceed this figure natural drying gives a cheap and satisfactory solution. Shortage of labour has necessitated the introduction of combine harvesting machines, and in order to make these machines pay during the short period they are used, they must be kept working intensively. This led to harvesting at a higher initial moisture content than previously, even at over 30% moisture. An extension of the grain dryer's capacity was therefore necessary, and a better constructional design sought. The design of a good grain dryer can only be obtained after the physical laws of water evaporation are known.

Research work in this direction has been done by many investigators. The names of Edholm,[1] Hirsch,[2] Mountfield *et al.*,[3] Hutchinson,[4] Oxley,[5] and Hukill[6] are well known in this respect. Probably the most extensive and thorough research is that of Simmonds *et al.*[7] Some results, obtained at the Government Laboratory for Drytechnical Research at Wageningen, differ, however, from the conclusions of the authors mentioned and a survey of these Dutch results may be of interest.

This paper will not discuss the construction of drying machines, but will consider the effect of conducting a hot air flow through a grain layer. This problem can only be approached if the drying conduct of a thin layer is known.

Theoretical considerations

It is customary to describe the moisture content as a percentage of the total weight of the grain (wet basis), but as this concept is very troublesome for calculations it is preferable to relate the moisture to the weight of dry matter (dry basis). Thus, material composed of 80 lb. of dry matter and 20 lb. of water has a moisture content of 20% (wet basis) or 25% (dry basis). Similarly, the moisture content of the air during drying will be expressed as a percentage of weight of the dry air, this figure being independent of variations in temperature or in barometric pressure.

When grain is exposed to a current of hot air, a double exchange will result. Heat is transferred from the air to the kernels and water evaporates from the grain to the air. The physical laws governing both processes show a great conformity. The heat-flow (per unit of time) is proportional to the difference in temperature between the air and the grain surface and to the area of this surface. The rate of evaporation is proportional to the difference in the pressures of water vapour between air and boundary layer as well as to the surface area. If all heat is used for evaporation, a relation similar to the well-known psychrometric formula will be found by equalizing the heat-flow to the evaporation, the latter multiplied by the latent heat of evaporation.

These relations are not suitable for calculating drying processes, as the surface (per unit weight of dry matter) is an unknown and practically immeasurable quantity. To overcome this difficulty the laws of evaporation should be studied first, and the heat transfer calculated from a heat balance.

When calculating the heat balance, the heat used in raising the temperature of the wheat must be remembered. The results of Disney[8] and our own figures are in agreement that the

specific heat of 100 g. of grain (dry matter) is $(37 + w)$ cal./°C (w being the moisture content on dry basis).

An important factor on the latent heat is the influence of lowering of the vapour pressure of water at the boundary layer. If this pressure amounts to p (its maximum value being p_{sat}), the latent heat ought to be multiplied by:

$$\left[1 - \left(\log_e \frac{p - p_o}{p_{sat} - p_o}\right)\right]$$

The increase due to overcoming adhesive forces is small and can be neglected in ordinary drying practice. The heat balance can be written therefore:

$$\frac{dQ}{dt} = C_1(\theta_a - \theta_{gr}) = C_2(37 + w)\frac{d\theta}{dt} - \left[1 - \log_e \frac{p - p_o}{p_{sat} - p_o}\right]\lambda \frac{dw}{dt} \quad \ldots\ldots\ldots\ldots\ldots \quad (1)$$

where λ is the value of latent heat for water at temperature θ_{gr}, and $\frac{dw}{dt}$ is negative.

For wheat and similar small-kernel grains, the temperature gradient within the kernel will be neglected. The small variations from barometric pressure of the drying air can also be neglected.

Rate of drying

At the Laboratory for Drytechnical Research, a considerable number of drying experiments have been conducted. It has been possible to evolve a generally applicable empirical law of drying by plotting drying curves for a number of agricultural products of widely differing types (grass, lucerne, clover, fodderbeet, parsnips, soya-beans, groundnuts, wheat, barley, oats, maize and linseed). If the drying rate is plotted against moisture content (on dry basis), the result will be three successive linear graphs, followed by a curve ; as this last stage is not reached in practical drying, it may be neglected. Here, theory and practice correspond to a surprising degree; for instance, when drying wet maize with 34–35% initial moisture content at 100 , the differences between calculated and determined values were not more than 0·5% at high and 0·25% at low moisture contents.

Former investigators considered the drying curve to be a pure logarithmic curve. According to our results the curve should be a combination of three sections of logarithmic curves running into each other at the intersecting points without a break. Fig. 1 shows that the difference between one or two such logarithmic curves is only small, if the moisture content after a certain time of drying is calculated, but when the time to reach a certain moisture content is considered, the difference is significant. This is the main problem.

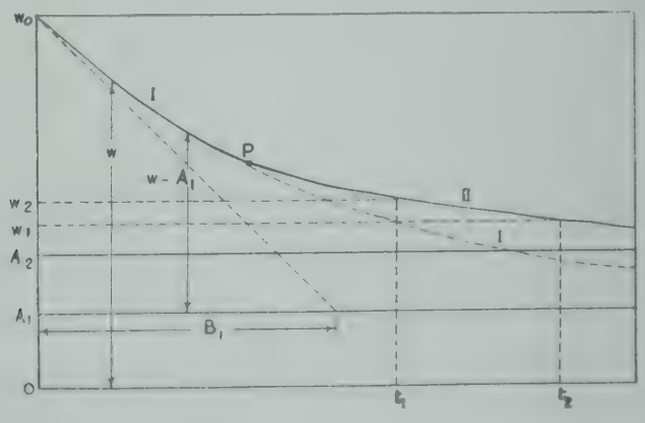

FIG. 1. *Sketch of two successive logarithmic drying curves*

$$\text{I} : \log_e (w - A_1)\Big] = -\frac{t}{B_1} + \log_e (w_0 - A_1)\Big]$$

$$\text{II} : \log_e (w - A_2)\Big] = -\frac{t}{B_2} + \log_e (w_{02} - A)\Big]$$

(w_1 and w_2 are the moisture contents of curves I and II after elapse of time t_1. t_1 and t_2 are the drying times required to reach moisture content w_1.)

Generally speaking, the drying curve corresponds with the formulæ:

$$\text{stage I} : \quad -\frac{dw}{dt} = \frac{w - A_1}{B_1}$$

$$\text{stage II} : \quad -\frac{dw}{dt} = \frac{w - A_2}{B_2}, \text{ etc.}$$

All three linear stages do not always appear, depending on drying temperature and initial moisture content. The first problem is to find an approximation for the Fig. 2 for given drying conditions, and in this connexion many drying curves were measured.

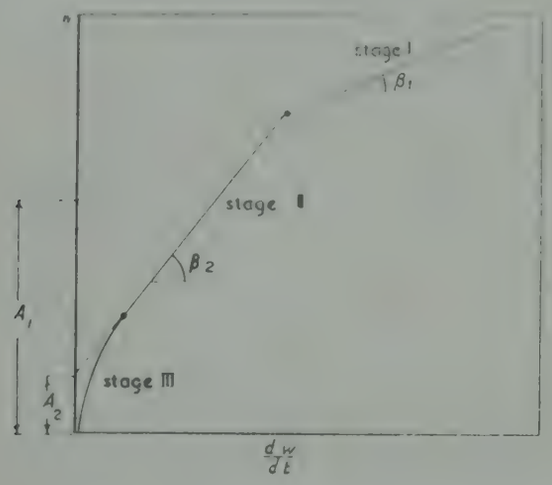

FIG. 2. *General scheme of a drying diagram*

$$-\frac{dw}{dt} = \frac{w - A_1}{B_1} \qquad tg\ \beta_1 = B_1$$

$$\frac{dw}{dt} = \frac{w - A_2}{B_2} \qquad tg\ \beta_2 = B_2$$

A sketch of the apparatus used is given in Fig. 3. A layer of wheat 1 cm. thick (about 3 kernels) was placed between two vertical metal screens, and weighed periodically.

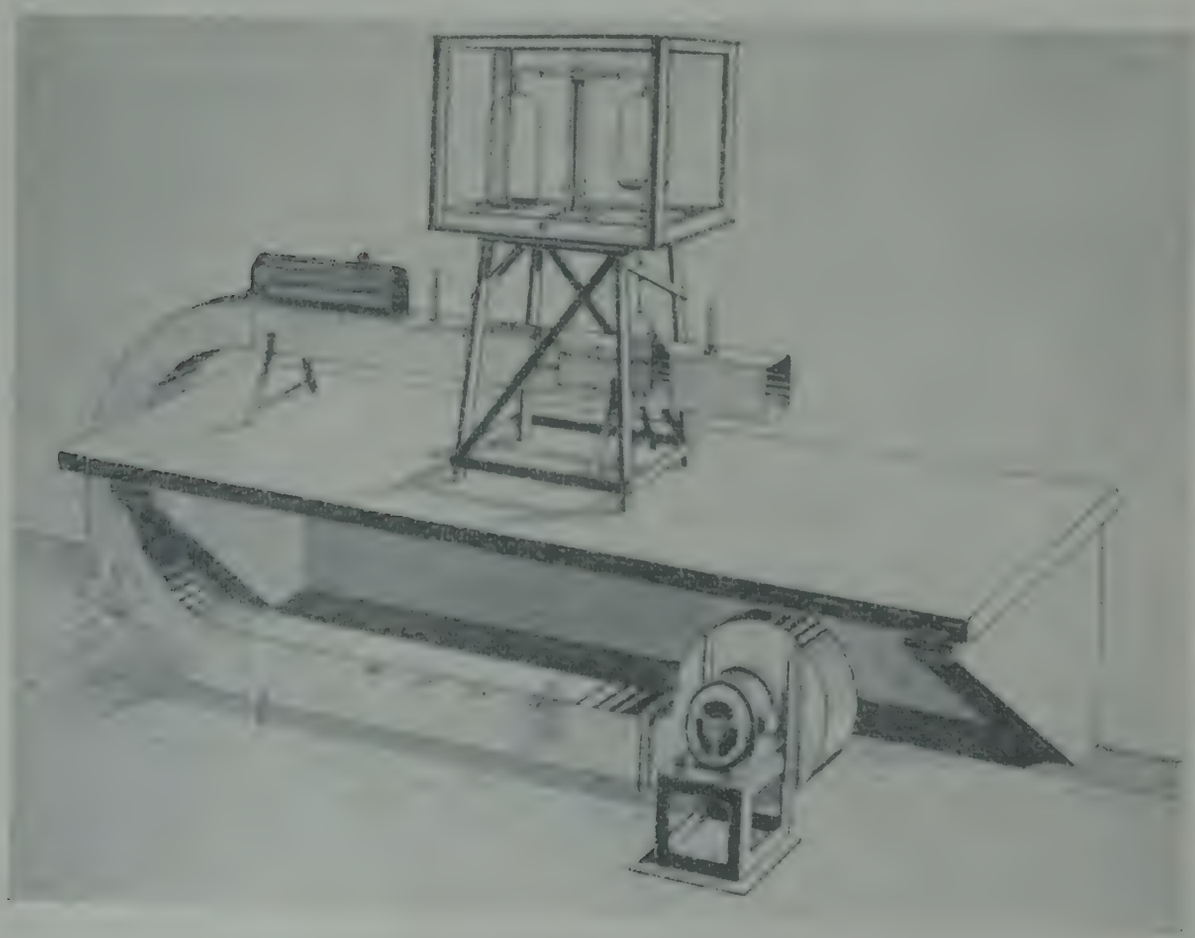

FIG. 3. *Arrangement used for the drying tests on grain*
Within the lower part of the duct is inserted an electric heater

Many variations of the arrangement were tried, such as drying within a stove. The only one which could be run without interruptions for weighing was that of Fig. 4, but it is not very suitable for experiments on grain.

FIG. 4. *Arrangement for drying tests without interruptions for weighing*

In order to measure the kernel temperature, a small hole was drilled through the kernel, and a small thermocouple was inserted (0·75 mm. diameter). The most convenient device was a hypodermic needle, through which an insulated constantan wire was passed and soldered at the edge. A compensating switching scheme was designed with an adjustable resistance so arranged that the temperature could be read to 0·1° on the accompanying scale.

In order to reduce as much as possible the time during which drying was interrupted, weighing of the grain and measurement of temperature were effected in simultaneous experiments on the same wheat, and the results were adjusted for time.

In order to work out the heat observations, variations of the temperature of the drying air had to be taken into account. This could be done by considering a coefficient α, defined by :

$$\alpha = \frac{\theta_a - \theta_{gr}}{\theta_a - \theta_w} \text{ or } \theta_{gr} = \theta_a (1 - \alpha) + \alpha\theta_w,$$

where θ_a = air temperature, θ_{gr} = grain temperature, θ_w = wet bulb temperature of the air $= 0{\cdot}25\,\theta_a + 9{\cdot}5°C$.

Values for $\log_e \alpha$ at various times are plotted in Fig. 5 from which it is evident that three stages occur. The first stage relates to a quick heating up of the air (1–1½ min.), the second one to a slower heating up of the grain kernel, whilst the third one corresponds with an equilibrium of heat transferred and heat used for evaporation. The second stage can with good approximation be represented by:

$$\log_e \alpha = -M - \frac{t}{N} : \text{ or } \alpha = e^{-M} e^{-t/N} = \alpha_0\, e^{-t/N} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

Values of the constants in equation (2) are shown in Table I.

The temperature difference between air and grain showed a similar trend (Fig. 6). It will be clear that the first (irregular) stage in Figs. 5 and 6 is due to heating of the air, which is a defect of the experimental method. This effect can be negatived by neglecting Stage I and only considering Stage II (the heating of the grain) from the commencement, at supposed constant air temperature (the curves have been extrapolated to zero time by continuing the lines for stage II to the ordinate).

Table I

Values of constants in equation (2)

θ_a	M	N	$\alpha_o = e^{-M}$	Duration of stage II		
				with respect to α	from $\theta_a - \theta_{gr}$	average
40°c	1·25	54·3	0·287	30·2 min.	31·8 min.	31·0 min.
60°c	1·36	8	0·257	8·0 ,,	7·6 ,,	7·8 ,,
80°c	1·34	6·3	0·262	6·0 ,,	5·5 ,,	5·75 ,,

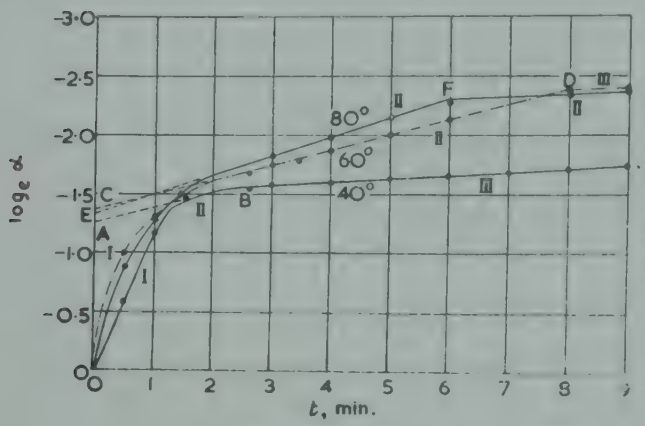

FIG. 5. *Experimental values of log* α

$$\alpha = \frac{\theta_a - \theta_{gr}}{\theta_a - \theta_w}$$

$$\log_e \alpha = f(t)$$

$$40°\ AB : \log_e \alpha = -1{\cdot}25 - \frac{t}{8}$$

$$60°\ CD : \log_e \alpha = -1{\cdot}36 - \frac{t}{8}$$

$$80°\ EF : \log_e \alpha = -1{\cdot}34 - \frac{t}{6{\cdot}3}$$

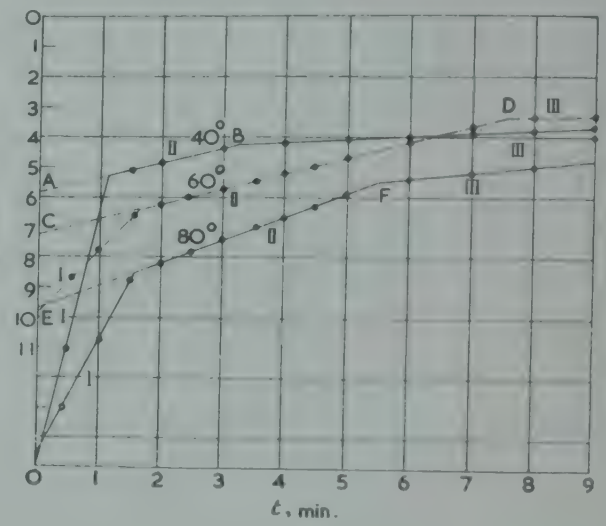

FIG. 6. *Experimental values of* $\theta_a - \theta_{gr}$

$$\theta_a - \theta_{gr} = f(t)$$

$$40°\ AB : \theta_a - \theta_{gr} = 5{\cdot}8 - \frac{t}{2{\cdot}03}$$

$$60°\ CD : \theta_a - \theta_{gr} = 7{\cdot}3 - \frac{t}{1{\cdot}95}$$

$$80°\ EF : \theta_a - \theta_{gr} = 9{\cdot}7 - t$$

It may seem peculiar that the period during which the kernels are heated is accompanied by an increased water evaporation. This is due to the large temperature difference between air and grain, resulting in a correspondingly greater heat flow, greater than that required to raise the grain temperature.

If the formulæ concering transfer of heat and of moisture are compared there appears a distinct similarity—as shown in Table II.

Table II

Similarity between evaporation and heat transfer formulæ

Evaporation	Heat transfer
$(w - A) = (w_o - A)e^{-t/B}$	$\alpha = \alpha_o e^{-t/N}$
$-\frac{dw}{dt} = \frac{w - A}{B}$	$-\frac{d\alpha}{dt} = \frac{\alpha_o}{N}$
$\log_e \frac{w_o - A}{w - A} = \frac{t}{B}$	$\log_e \frac{\alpha_o}{\alpha} = \frac{t}{N}$

These relations make it possible to draw, using the constants of Table I, the graph for the first evaporation stage, for which direct measurement is not possible because of irregularities owing to the short time elapsed.

It has been proved that the difference in shape between the first two stages in the drying graph is due to the heating of the grain. The next problem is the reason for the second break.

In order better to understand this second break, let us consider the vapour pressure–moisture equilibrium curve of the grain which was dried. Investigation led to the conclusion that this curve can be represented with sufficient accuracy by three intersecting straight lines.

At a point corresponding to 75% relative humidity (w = 18% wet basis at room temperature), there is a distinct discontinuity caused by a change of moisture distribution, the kernel surface becoming dry. Consequently, bacteria and moulds cannot continue their destructive activities at moisture contents below this point and they become dormant. Drying ought to be continued therefore to a lower moisture content than this. At this same point many properties of the grain change, such as shrinkage, volume weight, etc.

The scheme of a vapour pressure isotherm can be represented by Fig. 7 in which OU = $\frac{1}{2}p_{sat}$, QR = $\frac{3}{4}p_{sat}$, ST = p_{sat}, PQ is parallel to RS. Table III gives values of p_{sat} at various temperatures.

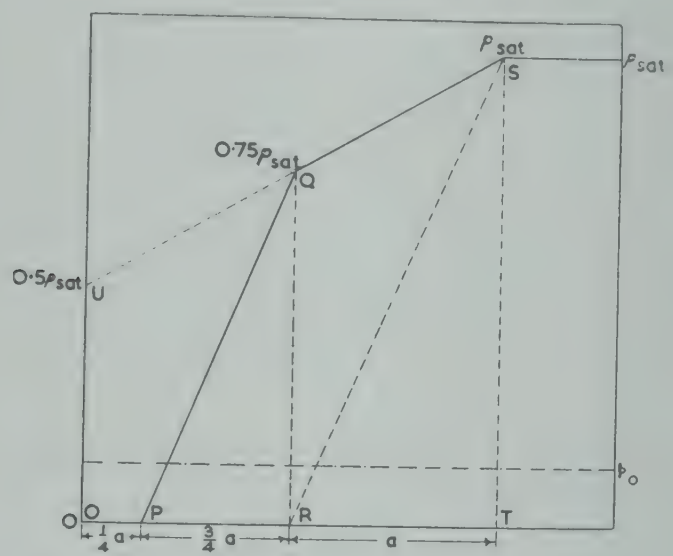

FIG. 7. *General scheme of a water-vapour isotherm for wheat*

Table III

Values of p_{sat} *and* a *corresponding with Fig. 7*

Temperatures θ, °C	80	70	60	50	40	30	20
p_{sat} (mm. Hg.)	355·1	233·7	149·4	92·51	55·32	31·82	17·54
a (% dry basis)	11·55	13·24	14·83	16·32	17·71	19·00	20.19

The velocity of evaporation is proportional to the differences of partial water-vapour pressures present at the kernel surface (boundary layer) and that of the drying air = p_0. From this it is concluded that Fig. 7 may be used as a diagram to represent drying speeds. If p_0 is deducted from the actual pressures, the result would be the drying graph, provided the moisture in the kernel is evenly distributed. This will certainly not be the case; a moisture gradient is present, shifting the situation of an arbitrary point to the right (for the mean moisture content of the kernel is higher than that corresponding with the surface moisture). As at the beginning and at the end of the drying process there cannot exist such a gradient, the corresponding points must be situated on the vapour pressure curve.

A better result than with vapour pressure curves could be obtained with a moisture equilibrium curve, showing the relative humidity as a function of a, such as Fig. 8.

It appears that the break points are situated on straight lines, that the second stage runs parallel with the base line RS, and that the graphs at the third stage pass through one point X at 0·6 a. We are, therefore, enabled to draw any curve for wheat having a low moisture content. The value of B at Stage II is governed by $B = a(1 - \varepsilon)$ (a function of temperature), divided by $p_{sat} - p_0$, by the coefficient of mass transfer and by the surface per 100 g. of dry matter $k_g a_m = 0{\cdot}000211\ (w_0 + 6{\cdot}07)\left(1 - \frac{p_{sat} - p_0}{625}\right)$ (= evaporation min mm Hg). This relation makes it possible to fix the scale of drawing. It is apparent that the second break occurs at a value of about 17·5% R.H. or 0·175 ($p_{sat} - p_0$). During this stage a different

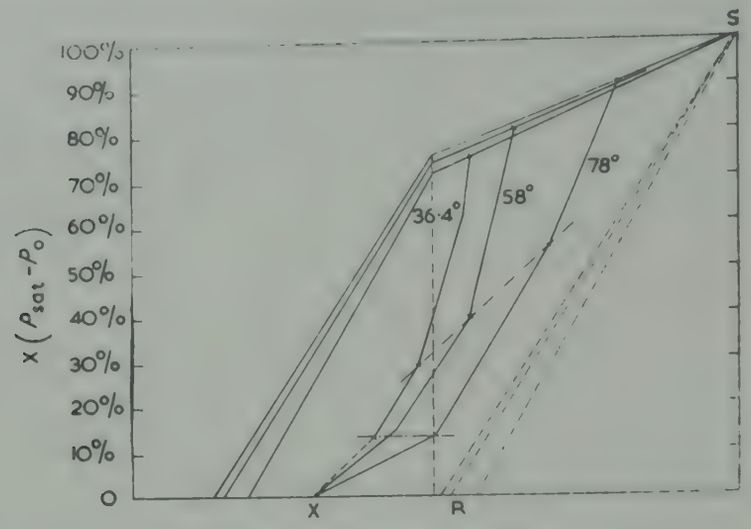

FIG. 8. *The moisture-equilibrium curve used as an aid to represent dynamic drying phenomena*

θ °C	p_{sat}, mm. Hg	p_0, mm. Hg	$\frac{p_0}{p_{sat}}$	a, %w
78	327·3	7	0·0214	11·89
58	136·1	7	0·0514	15·13
36·4	55·6	7	0·1537	16·82

law of evaporation must be in force, which is clearly explained in the recent book of Krischer.[9] It should be borne in mind that the first stage is due to heating of grain. If the grain at the commencement has a temperature only a few degrees lower than the drying air, Stages I and II will coincide.

Next to be considered is the drying behaviour at high initial moisture contents. Many experiments were carried out on this point, but as they were executed during winter, the grain had to be moistened first. The results showed clearly that such premoistened grain has a much higher water evaporation rate (e.g., $-\frac{dw_0}{dt} = 2{\cdot}46$) than that of the original grain and the data obtained could not be used. The swelling of the kernels seems to play an important role in the speed of evaporation.

An attempt has also been made to derive a formula for the drying of agricultural products of high initial moisture content, such as green crops.[10] In order to obtain a similar knowledge regarding the drying of grain, the behaviour of a thin layer during the drying process must first be known.

Conclusion

This report is meant as a contribution to the problem, but a great deal of further research will be necessary, before the correct solution can be given.

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SESSION V

Chairman : Dr. M. Pyke

THE EFFECT OF DRYING AND STORAGE IN THE DRIED STATE ON SOME PROPERTIES OF THE PROTEINS OF FOOD

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(Torry Research Station, Aberdeen)

Introduction

Although the proteins of food are known mostly on account of their nutritional significance, they probably have an equal importance in imparting characteristic physical properties to many foods. In flesh foods such as meat and fish, proteins are the main structural components and are organized into predominantly fibrous forms which are very different from those present in other, non-fibrous yet mainly proteinaceous tissues such as liver or kidney. Proteins, either as individuals or as liaisons with other molecules, are responsible in foods like eggs, milk, gelatin and their products for important properties such as the capacity to gel, coagulate, thicken, emulsify and foam. Impairment of these desirable properties and consequent reduction in food quality can often be attributed to alterations in the proteins of the commodity. In fact, the problem of retaining acceptable eating quality in proteinaceous foods, particularly as regards texture, is very largely the problem of ensuring the stability of particular proteins.

Food-drying processes are certainly capable of impairing quality through their effects on proteins. Drying usually involves the application of heat, and proteins are among the most heat-labile of substances. (It remains true that in a limited number of cases the application of heat may result in improved quality such as the coagulation attending ordinary cooking, the conversion of connective-tissue collagen into gelatin, the enhanced digestibility of certain seed proteins[1] or the improvement in baking quality of non-fat dry milk solids.[2]) The difficulty of drying proteinaceous foods has stimulated considerable research into improved methods with the aim, generally speaking, of lessening the destructive effect of heat. Spray drying is now the method of choice in the production of high-quality dried egg and milk products. Warm-air tunnel drying has been used successfully for the drying of pre-cooked meat[3] and fish[4] minces, but is not feasible for whole pieces of flesh. For the latter, radically different techniques must be used, usually a vacuum process;[5–8] even the freeze-drying process, which is perhaps the gentlest way of drying proteins, is being explored.[9,10]

Despite many improvements in drying techniques, most dried products are still some way from fulfilling the ideal requirement of being indistinguishable from the starting material after reconstitution. Of course, for some uses it is not necessary to meet this requirement, for example where the dried product is to be incorporated into a mixture or a 'made-up' dish. The most obvious difference between a reconstituted dried product and its fresh counterpart lies in the difference in texture, which are probably attributable to alterations of protein. For instance, reconstituted dried whole milk has a rough 'tactual' feel in the mouth;[11] dried egg has very little or none of the foaming power of fresh egg[12] and most dehydrated meat and fish products taste distinctly drier and tougher after reconstitution than the undried materials.

Allied to the problems of attaining successful drying conditions are those of arresting deterioration during storage in the dried state. Most of the work on the storage deterioration of dehydrated proteinaceous foods has been concerned with the elimination of the off-flavours and discolorations resulting from non-enzymic 'browning' reactions; textural changes have received only passing attention. It seems likely, however, that problems of textural deterioration during storage will receive more attention now that some progress is being made towards preventing the development of off-flavours. The texture of dehydrated fish (vacuum-contact dried[6, 7] or frozen-dried), for example, quickly becomes drier and tougher after only moderate storage; most of the results reported in this paper have been obtained from this material.

For an understanding of the changes suffered by proteins during drying and storage and their relationship to alterations in the properties of food, it is necessary to have some idea of the relationship between the structure of proteins and the gross properties which they confer on the foodstuff. The problem is complicated by the fact that foods contain a multiplicity of proteins having diverse properties, but some approach may be made by considering briefly certain basic known features of protein structure in relation to the properties of foods.

Protein structure

The primary structure of proteins is a polymeric chain of fifteen or so α-amino-acids joined together through peptide bonds involving the α-amino- and α-carboxyl-groups of the amino-acids. The amino-acid residues of different proteins are arranged in different sequences which results in different arrangements of reactive side-groups along the peptide chains. For a number of reasons it is clear that in native proteins this chain must be coiled or folded back upon itself and the most likely fold so far proposed is a helix having 3·7 amino-acid residues per turn. The helix is stabilized by the maximum number of hydrogen bonds between the carbonyl and imino groups of the peptide primary structure and contains no side groups in its core. It seems likely that not every part of every protein molecule conforms to this α-helix pattern, but it forms a useful basis for discussion. Corpuscular or globular proteins must consist of several helices held closely together by a variety of possible bonds including electrovalent bonds between polar groups of side chains, hydrogen bonds, van der Waals' attractions between non-polar side groups and covalent bonds. The only well-authenticated bond of the last type is the disulphide bond. It has been pointed out[13] that since the hydrogen bond is electrostatic in nature it ought perhaps to be considered along with electrovalent bonds as ordinarily understood.

The specific folded arrangement of the native protein molecule may be easily disrupted by a variety of agents like heat, extremes of pH, surface forces, and organic solvents; the process is generally known as denaturation. This spatial rearrangement is accompanied by several characteristic alterations in properties including reduced solubility, increased asymmetry of the molecule, loss of ability to crystallize, loss of biological activity, increased reactivity of side groups especially disulphide and sulphydryl groups. The amount of unfolding in most denatured protein is only moderate, but must extend in part at least to the α-helices since the *X*-ray diffraction pattern of these helices changes with denaturation to a β-pattern. The structure of the β-protein is thought to be that of a fully-extended peptide chain in a pleated ribbon arrangement.

With appropriate condition of ionic strength and pH, the denatured protein usually becomes insoluble and often coagulates. This latter process is probably an intermolecular aggregation resulting from the interaction of side chains which in the native molecule are sterically masked in the internal volume of the protein and which are brought to the surface in the course of denaturational unfolding.

Relationship of structure to properties

Only a few qualitative observations are possible. For example, a pre-requisite for the formation of a stable gel is a thread-like, or at least very asymmetrical, molecule capable of cross-linking with itself.[11] The native proteins of egg white and of meat and fish must be partly of this type.

Foaming or aerating ability in fresh egg white is probably associated with the capacity of its proteins to unfold into something approaching a monolayer and thus stabilize the air–fluid interface. A protein molecule with a more or less loose internal cohesion would seem to be indicated.

The fibrous eating quality of meat is a reflection of the fibre structure of the muscle cell which itself derives from the predominantly fibrous structure of the chief muscle proteins—myosin and actin.

Alterations to protein during drying and subsequent storage

(*a*) *General*

The mechanisms by which proteins are altered during drying seem likely to be different in some particulars from those occurring during storage, but in the present state of knowledge it hardly seems justifiable to discuss drying and storage separately.

Generally speaking, proteins are very susceptible to alteration during ordinary drying techniques and usually methods like freeze-drying, which avoid the use of heat and agitation, must be used. Many proteins have in fact been freeze-dried without obvious denaturation and appear to be stable indefinitely in the dry state,[15] but there are reports that at least two food proteins—egg albumen[16] and rabbit myosin[17]—cannot be even freeze-dried. (Small bundles of frog muscle fibres, on the other hand, have been freeze-dried without entirely losing their contractility.[18]) It is also probable that some of the lipoprotein constituents of food cannot

be dried, however carefully, without alteration, since serum β-lipoprotein is unstable to freezing and freeze-drying.[19] Lea[20] has recently reviewed a number of deteriorative changes in lipoproteins, most of which involved the lipid moiety. Any of these changes in lipoproteins might occur during drying and storage and have an effect on quality; the present discussion will be confined to unconjugated proteins.

(*b*) *Agents causing protein alteration*

The principal agent is certainly heat, although the effect of surface forces during spray drying, for example, cannot be entirely discounted. During drying, the concentration of tissue components, like inorganic salts, may rise to a level which is damaging to the protein, and the translocation of potassium in the cell during the drying of meat has been proposed[21] as one of the factors causing denaturation.

(*c*) *Denaturation without insolubilization*

Although there is no published account of work on this point, it is possible that denaturation *per se*, that is a configurational rearrangement, would have an effect on food quality, for example through an increase in viscosity or reduction in solubility. Apparently some spray-dried egg powders have poor aerating power even though the solubility of their proteins as usually determined is unimpaired.[22] This could mean that the egg proteins have become moderately unfolded and 'set' in configurations which no longer allow the more complete unfolding necessary to stabilize a foam. It is known that denatured proteins cannot be as readily spread in the form of a monomolecular layer as native proteins.[23]

(*d*) *Insolubilization*

There is a good deal of evidence to show that the insolubilization of the proteins of milk[21] and eggs[22] is associated with a deterioration in qualities such as aerating power, thickening and emulsifying power, and cake leavening ability. Preliminary experiments[24] have suggested that the development of toughness and decrease in swelling ability during the storage of dehydrated fish are correlated with decreases in protein solubility. No attempt to explain these correlations in terms of structural or other alterations has yet been made.

Of the many possible mechanisms that lead to insolubilization there are only two which are supported by experimental evidence: (i) 'browning' reactions and (ii) the interaction of denatured protein molecules.

(i) '*Browning*' *reaction.*—The reaction of carbonyl compounds, usually carbohydrates, with the amino-groups of proteins has been implicated in the development of insolubility during the storage of dried egg,[25] milk[26] and beef.[27] The loss of amino-groups in a protein would of itself probably lead to insolubility through loss of polar properties, but the effect of substituting a sugar residue, for example, for an amino-group is problematical. Apparently the initial condensation reaction of sugar and protein can occur without insolubilization.[25] Bate-Smith & Hawthorne[25] suggest that a secondary rearrangement of the *N*-glycoside structure, presumably first formed, to an *iso*glycosamine-type structure is necessary for insolubility, but there seems no good reason why a protein substituted with such a rearranged residue should be less soluble than a protein substituted with an *N*-glycoside residue. It is probable that the residue, modified or not, serves as a reactive focus through which the protein aggregates. It has been demonstrated[28] that the average molecular weight of bovine serum albumen increases during the 'browning' reaction in solution between it and glucose. This observation and similar ones using formaldehyde[29] and acetaldehyde[30] as reactants was interpreted as indicating some cross-linking between the protein molecules, a process which, if carried far enough, could obviously lead to insolubility.

A reaction which has analogies with the 'browning' reaction is the tanning, particularly the formaldehyde tanning, of leather collagen, in which the stability and tensile strength of the protein are markedly increased. Evidence has been presented[31] which suggests that in the case of formaldehyde tanning at least, these alterations are the result of the formation of methylenic cross-links. Decreases in swelling capacity and fibre extensibility accompany the storage of dehydrated fish and it is possible that in this case cross-links are being formed through the intervention of non-protein tissue constituents or their degradation products. Gustavson[32] has speculated that self-tanning of proteins may occur through the oxidation to quinones of the aromatic side groups of one protein molecule which then 'tans' another protein molecule. Such a reaction also may have importance in food processing.

(ii) *Interaction of denatured protein molecules.*—As mentioned above, the denaturation of most proteins in solution results in the formation of an insoluble precipitate or coagulum, and it is probable that part, or in some cases all, of the insolubilization accompanying drying and storage is due to the interaction of denatured proteins. Certainly in dehydrated fish insolubilization can occur without visible ' browning ',[24] and there are several reports of purified proteins becoming insoluble when heated alone in the ' dry ' state, for example, egg albumen,[33, 34] soya-bean globulin, casein, zein and wheat gluten.[35]

The nature of the bonds which hold insoluble aggregates of denatured protein molecules together cannot be very different from those imparting stability to the native molecule. Intermolecular salt bridges between denatured protein molecules have been proposed,[36] as have intermolecular hydrogen[37, 38] and disulphide[38] bonds. Waugh[39] suggests that it is not plausible to explain insolubility on the basis of intermolecular hydrogen bonds involving many main-chain peptide groups[40] and favours instead the idea of van der Waals' interactions between large non-polar side groups. All these bond-types have been thought of particularly in relation to the aggregation of proteins in aqueous solution when covalent-bond formation (except disulphide-bond formation) is unlikely to occur. In the dry or near-dry state, however, covalent-bond formation may occur quite extensively, particularly at high temperatures. For example, marked diminutions in the numbers of acidic and basic groups of several pure, dry proteins occur when they are heated;[35] ester and amide links are probably formed. Of significance for the storage toughening of dehydrated fibrous foods like meat and fish are the several instances of increases in fibre strength which result from heating systems like collagen,[41] fibrin film[42] and synthetic protein fibres.[43] These alterations in physical strength have all been attributed to the formation of additional covalent cross-links.

Alterations to fish muscle proteins during drying and storage

Recently an attempt has been made[24, 44] to elucidate some of the changes in the proteins of fish flesh during various kinds of dehydration process and during storage in the dried state. Although made with particular reference to fish, it is thought that the following observations will have importance in the drying and storage of other protein foods.

(*a*) *Alterations during drying*

Even freeze-dried fish fillets, which are the best product so far examined, are noticeably tougher and drier in texture after reconstitution than fresh fish. In the dried fish the protein gel system of the fresh fish is much disorganized even though the microscopical appearance of the muscle cell is unchanged. The true water-binding capacity of the proteins is, for example, greatly reduced. The solubility of the proteins of freshly prepared dehydrated fish in 0·5M-potassium chloride pH 7·0, as determined by a standard technique, is very much less than that of the proteins of fresh fish (Table I) and this fact, together with a reduced ATP-ase activity,[45] indicates that the main structural protein complex of muscle, actomyosin, has been denatured on drying. This is not surprising since actomyosin is one of the most unstable proteins known.

The solubility of the dried fish is much greater in solutions of reagents like urea and guanidine hydrochloride (Table I) which are known to have the property of readily forming hydrogen bonds and which are thought to prise apart peptide chains previously hydrogen-bonded and so render them soluble. Lithium bromide and formamide are also said to have this property, but in a reduced degree, which probably explains why they are less effective with dried fish. The solubility of the proteins is even greater when the solutions of hydrogen-bond-breaking substances are supplemented with reagents like thioglycollic acid and monothioglycol which are known to reduce (split) disulphide bonds. The inference is that the protein of the dried fish is stabilized partly by hydrogen bonds and partly by disulphide bonds.

Since the protein is not completely soluble in solutions of hydrogen-bond-breaking plus reducing substances, possibly other bond-types are involved. The solubility in the detergent, sodium dodecyl sulphate, is very high, that in sodium salicylate less so; detergents are known to bind very strongly and to solubilize many native and denatured proteins. Presumably the dehydrated fish protein fragments solubilized by detergent still contain unreduced disulphide bonds.

From a recent study of the swelling and elastic behaviour of air dried cuttle-fish flesh, Kishimoto *et al.* have similarly concluded[46] that the protein network of the water-swollen material is at least partly cross-linked by hydrogen bonds which can be broken by the action of urea

solutions. Woods[47] also found that the air-drying of actomyosin films is accompanied by the formation of stable cross-linkages which reduce the elasticity and swelling in water of the films.

Table I

Solubility of the proteins of fresh and dehydrated fish (various batches of vacuum-contact dried cod)

	Soluble protein as % of total protein of sample	
	fresh	dehydrated
0·5M-KCl*	>90	16 (2·3†, 5)
50% urea in water	>95	44 (4·9, 6)
50% urea in 0·1M-thioglycollate		66 (4·0, 4)
50% urea in 0·1M-monothioglycol		67
8M-guanidine hydrochloride		49
5% sodium dodecyl sulphate		90
0·5M-sodium salicylate		50
8M-formamide		22
M-lithium bromide		25

* All the reagents are at pH 7·0–7·5.

† The figures in parentheses are the standard deviation and number of samples, respectively. All the other results refer to one sample only, except that for sodium dodecyl sulphate which is the mean of two samples.

The formation of covalent links involving the amino and carboxyl side groups should lead to a diminution in the total acidic and basic groups of the protein, but determinations[44] using the dye-binding method[48] showed that dehydrated fish differed but little from fresh fish in this respect. Difficulties were encountered when an attempt was made to estimate sulphydryl contents by various methods, but the evidence suggested that the sulphydryl content of dehydrated fish was slightly less than that of fresh fish, which is as might be expected if disulphide bonds are being formed.

(*b*) *Alterations during storage*

Apart from the difficulty of finding techniques which can estimate real molecular-structural differences between fresh and dehydrated fish, there is the difficulty of correlating the results with differences in textural eating quality. This is because the textural quality of a fibrous material like fish is composite in nature, partly attributable to the gross ' histological ' structure and partly to the molecular structure of the material. This difficulty is absent when alterations in texture during storage in the dried state are considered, since the ' histological ' structure is fixed and any change can be due only to alterations in molecular structure.

Depending mainly upon the temperature and moisture content, dehydrated fish becomes progressively tougher and drier in texture during storage.[1, 49] This behaviour can be interpreted as indicating the progressive formation of rather firm cross-links between the individual molecules of the protein gel network; it is not necessary to assume that the molecules involved are denatured, although in this case they probably are. The development of increased strength and rigidity in polymer networks is also associated with an increase in crystallinity or alignment of the individual chains,[50] but this process would seem to be inherently improbable during storage of fish protein where increased temperature leads to increased toughness; the reverse would be expected if the toughening process were a crystallization.

Some evidence for the formation of new cross-links has been obtained from measurements of extensibility, swelling and solubility of stored dehydrated fish and an attempt has been made to elucidate the underlying chemical changes.[24] Most of this work has been done on products heated at temperatures (50° and 80°) well above those normally encountered in the storage of foods. It has not been proved that the deteriorative processes are the same at these high temperatures as at normal temperatures; the assumption is made that they are.

(i) *Changes in extensibility during storage.*—Bundles of muscle fibres 1–2 mm. in diameter and about 1 cm. long were removed from blocks of dehydrated fish and freed as completely as possible from visible connective tissue. They were reconstituted and suspended in dilute neutral buffer held at a constant temperature and weighted in steps. At each step the elongation and diameter of the bundle were measured with a travelling microscope and the percentage elongation and tension calculated from the unweighted length assuming the bundle to be solid. Three or four bundles from different parts of each block were examined in this way.

The bundles were not perfectly elastic and suffered a permanent deformation on stretching, but up to about 10% elongation there was an approximately linear relationship between tension and elongation (Fig. 1). All the samples from which the bundles were taken were graded for texture after cooking by a group of six people who found that the freshly prepared freeze-dried cod, that heated for 12 hours and that heated for 24 hours, were, respectively, slightly tougher, much tougher and very much tougher than fresh fish. There is a marked decrease in extensibility with the tougher, more strongly heated samples amounting to an approximately threefold increase in 'elastic' modulus when passing from the freshly prepared to the more strongly heated sample. Part of the elasticity of the fibre bundles is probably due to the extremely thin sarcolemma which surrounds each fibre, but it hardly seems possible that changes of the magnitude recorded here could be caused solely by changes in the extensibility of this structure.

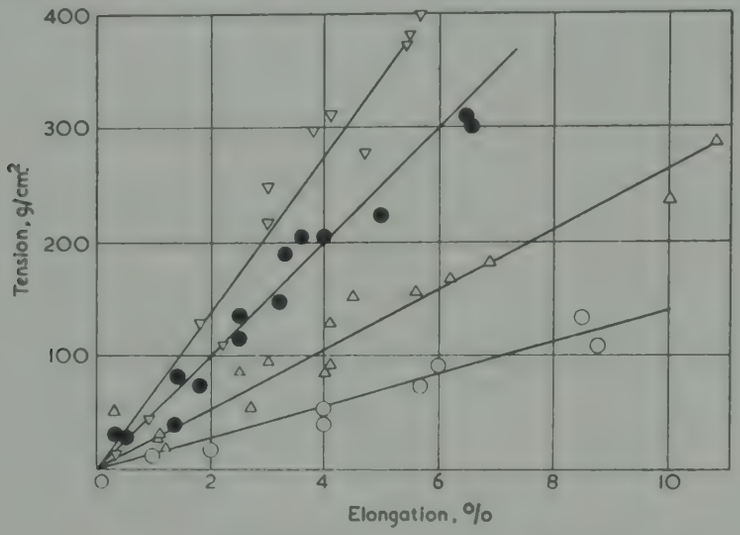


FIG. 1. *Elongation–tension diagrams of fibre bundles from fresh, dehydrated and heated dehydrated fish*

○ Fresh cod
△ Freeze-dried cod
● Freeze-dried cod heated at 100°, 30% moisture, 12 hours
▽ Freeze-dried cod heated at 100°, 30% moisture, 24 hours

(ii) *Changes in swelling during storage.*—The degree of equilibrium swelling of a polymer network in a given solvent is a relative measure of the degree of cross-linking.[51]

Blocks of vacuum-contact dried cod of various moisture contents were heated in nitrogen at 50° for various lengths of time and their tenderness and degree of swelling determined. Tenderness was in this case measured by a trained taste-panel and degree of swelling by a standard procedure (Table II). In all cases there is a decrease in the degree of swelling with the length of storage and this decrease shows a general inverse correlation with the taste-panel tenderness score. In addition, the experiment indicates that increasing the moisture content of the sample leads to a more rapid rate of development of toughness and of decrease in swelling.

Table II

Degree of swelling and tenderness of stored vacuum-contact dried cod fillets

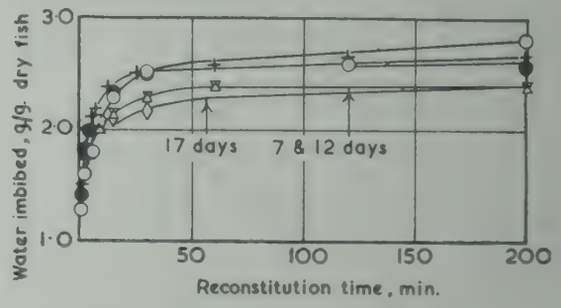
Moisture in sample, %	Days heated at 50°	Tenderness* score	Degree of swelling†
—	0	2·8	7·27
4·4	2	2·9	7·10
3·9	4	3·4	6·98
4·3	16	3·6	6·33
6·2	2	3·3	6·93
6·1	4	3·5	6·84
6·2	16	4·0	6·73
11·1	2	5·3	6·97
11·8	4	4·9	6·53
10·9	16	6·4	6·46

* Taste panel scores run from 0 (tender) to 8 (very tough).
† Arbitrary units.

Another demonstration of decreased swelling and water-holding capacity during storage was furnished by an experiment in which the degree of reconstitution was measured, that is the amount of water imbibed under standard conditions by whole blocks of dehydrated fish (Fig. 2). The fish were stored at 80° and 3·0% moisture content for periods of 2, 4, 7, 12 and 17 days. A group of six people graded these samples in order of toughness, and the 'average' order which emerged was as follows: 0, 2; 4, 7 and 12 together; 17 days; the first being the least tough.

FIG. 2. *Reconstitution of vacuum contact dried cod heated at 80°, 3% moisture*

○ unheated
+ heated 2 days
● „ 4 „
Δ heated 7 days
▽ „ 12 „
◇ „ 17 „



(iii) *Solubility changes during storage.*—The solubility of the proteins of dehydrated fish decreases in all the solvents examined (Fig. 3). The rate of this decrease is, however, different for different solvents and is particularly marked for the alkaline (pH 12) (Fig. 3) and for the detergent (Table III) solutions. The decrease in solubility does not occur solely in the KCl-soluble portion since the solubility in urea solutions falls in samples from which the KCl-soluble portion has been removed before heating. It would seem that the only reasonable explanation for the marked reduction in solubility in such powerful protein solvents as alkali and detergent is the formation of stable intermolecular cross-links.

FIG. 3. *Solubility of vacuum contact dried cod heated at 50°, 3% moisture*

○ amount soluble in 0·5 M-KCl
● „ „ „ 50% aqueous urea
Δ „ „ „ 50% urea in 0·1 M-thioglycollate, pH 7
▽ „ „ „ NaOH, pH 12

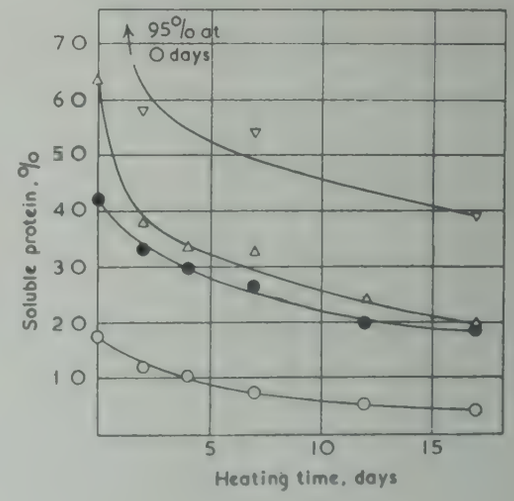


Table III

Solubility of stored vacuum-contact dried cod fillets

Moisture content, %	Days heated*	% Soluble protein of total protein in sample: Urea–thioglycollate†	Detergent‡
—	0	90	65
6·2	2	74	51
6·1	4	58	48
6·2	16	48	42
11·1	2	65	47
11·8	4	51	40
10·9	16	38	38

* All the samples were heated in nitrogen at 50°.
† 50% urea in 0·1M-thioglycollate pH 7.
‡ 5% sodium dodecyl sulphate pH 7.

With the heated samples there is a progressive reduction in the capacity of thioglycollate to render the urea-treated protein more soluble and this behaviour is interpreted as meaning that changes in the reducible disulphide bonds of the protein are occurring during heating. It is known that when wool keratin is heated under neutral or alkaline conditions, its disulphide cross-links are altered to the non-reducible thioether (—S—) form and a new thioether-linked amino-acid, lanthionine, appears in hydrolysates of the heated protein. The reaction occurs more rapidly as the conditions are made more alkaline, but appreciable reaction does occur at neutrality.[52] It was therefore of interest to look for lanthionine in hydrolysates of heated dehydrated fish. Using a combination of ion exchange and paper chromatography, no lanthionine could be detected in hydrolysates of fresh fish, freshly prepared dehydrated fish or stored, very tough dehydrated fish (heated for 12 days at 80°, 3% moisture content), but unequivocal trace amounts have been found in hydrolysates of severely treated dehydrated fish (heated at 33% moisture and 80 for 3 weeks). The conversion in dehydrated stored fish of small amounts of disulphide to thioether cross-links may have a bearing on the development of toughness, because although no new cross-links are introduced, the thioether link may impose restraints on the system which prevent it from swelling and distorting as easily as the more flexible disulphide links allow.

(iv) *Chemical changes during storage.*—So far, few chemical changes have been detected in stored samples which might indicate that reactive groups in the protein are involved in the formation of new cross links.

There is a decrease in sulphydryl content during storage as indicated by determinations made with *N*-ethylmaleimide, both in the sample itself and in the sample treated immediately before the determination with concentrations of urea that exert a powerful unmasking effect on ' hidden ' sulphydryl groups (Table IV).

Table IV

Sulphydryl content of stored vacuum-contact dried cod fillets (3% miosture content)

Days at 50°	Sulphydryl content (mg. -SH/100 g. protein)	
	Sample alone	Sample treated with urea
0	0·17	0·28
2	0·12	0·19
4	0·12	0·19
7	0·12	0·17
12	0·11	0·16
17	0·11	0·13

On the other hand, no difference in sulphydryl groups between the same samples was observed when the determinations were done with Barrnett & Seligman's reagent[53] (2 : 2′dihydroxy-6 : 6′-dinaphthyl disulphide) according to Flesch *et al.*[54] Similar anomalies arising from the use of different sulphydryl reagents have been encountered with dehydrated fish samples.[44]

Determinations on samples stored until they were extremely tough showed that the acidic and basic groups of the sample did not differ significantly from the values obtained on unstored samples. This was true of determinations by the dye-binding method[48] (Table V) which determines only protein groups, and titration with acid and alkali of the entire acidic and basic groups of the samples (Table VI). In addition, the basic groups determined by titration with perchloric acid in glacial acetic acid[55] and the available lysine content determined with fluorodinitrobenzene[56] were 23·6 and 23·6 equivalents 10^4 g. sample and 5·4 and 5·7%, respectively, for unheated and heated (12 days at 6·4% moisture, 80°) samples of vacuum-contact dried cod.

Table V

Acidic and basic groups of stored and unstored vacuum-contact-dried cod fillets by the dye binding method

Days at 50° (3% moisture content)	Acidic groups (equivalents/ 10^4 g. protein)	Basic groups (equivalents/ 10^4 g. protein)
0	17·2	13·7
2	17·9	13·5
4	17·4	13·8
7	17·8	13·3
12	16·9	13·1
17	17·5	13·1

Table VI

Titration of stored and unstored vacuum-contact dried cod fillets

pH	Moles H^+ bound/10^4 g. dry sample		pH	Moles OH^- bound/10^4 g. dry sample	
	Heated*	Unheated		Heated*	Unheated
5·54	2·7	2·7	8·22	2·7	2·7
5·14	5·3	5·5	9·43	5·2	5·4
4·74	8·0	8·1	10·10	7·5	7·7
4·21	10·5	10·8	10·50	9·8	9·9
2·94	17·0	17·0	11·28	14·0	15·0
2·37	19·0	20·0	11·65	14·0	17·0
2·06	21·0	20·0	11·91	15·0	18·0
1·58	20·0	21·0	12·33	14·0	12·0

* Heated at 6·4% moisture and 50° for 8 days.

Regier & Tappel[27] have found a progressive decrease in the formol titre of stored freeze-dried beef. Using their method, a similar decrease was found with stored vacuum-contact dried cod. It is suspected, however, that this decrease was not real but rather reflects the different solubilities of the samples since, on equilibrating the samples after each addition of alkali, the results were much the same for all the samples (Table VII).

Table VII

Formol titration of heated and unheated vacuum-contact-dried cod fillets

	% soluble protein of total protein of sample			Equivalents of $-NH_2/10^4$ g. protein	
	0·5M-KCl	50% urea	50% urea thioglycollate	immediate titration	equilibrium titration
Unheated	20	46	65	8·6	9·7
Heated A*	14	35	42	8·2	10·2
Heated B†	13	31	40	7·2	9·7

* 16 days at 50°, 6% moisture content.
† 4 days at 50°, 11% moisture content.

(v) *Other changes during storage.*—It has been found that the *X*-ray pattern of stored toughened dehydrated fish shows the presence of β-protein. Fresh fish dried to room humidity shows only the presence of α-protein. β-Protein is observed in stretched keratin or myosin threads and, as mentioned before, in orientated denatured proteins. Its structure is fundamentally different from that of the helical α-protein in that the principal hydrogen bonds are between adjacent peptide main-chains. β-Protein is less extensible than α-protein, a fact which may have significance for toughening during storage.

Lundgren & Binkley[57] have found that the fluorescent dye Rhodamine-B, whose red form is stabilized by substances which hydrogen-bond with it, binds to denatured but not to native proteins. This phenomenon is possibly indicative of a release during denaturation of hydrogen-bonded centres in the protein molecule which then become available for binding with the dye. This speculation suggested that it might be possible to detect differences in the degree of hydrogen bonding between, for example, stored and unstored dehydrated fish protein, but no change in the Rhodamine-B-binding capacity of dehydrated fish occurred when it was stored until very tough (Fig. 4, p. 176).

Conclusion

The reactions underlying textural deterioration in foods are obscure. It is possible that the chemical changes are too small to be measured by the present methods. It has been pointed out,[58] for example, that the cross-linking introduced by as little as 0·003% of divinylbenzene converts polystyrene from a soluble into an insoluble gel-like product. Such minute amounts of cross-linking would be very difficult to detect chemically.

In many protein foods the empirical relationships between rate of textural deterioration and temperature or moisture content remain to be determined. Other storage factors may be important, for example, ionic environment, pH, and oxygen content. Calcium is said to have a marked effect on the water-binding capacity and gelling power of meat[59] and on the plasticity of muscle fibres;[60] it too may have a role in deterioration during drying and storage. The interesting fact that toughening during storage is less with precooked than with raw dehydrated beef[49] may also hold some clue.

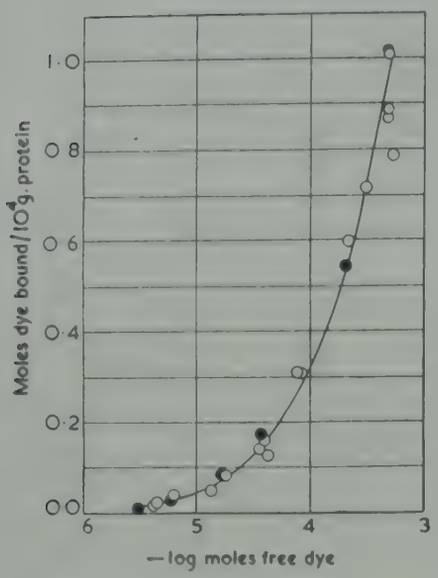


FIG. 4. *Binding of Rhodamine-B to vacuum-contact-dried cod*

○ unheated
● heated at 50°, 11·8% moisture, 8 days

Acknowledgment

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Discussion

Mr. E. J. Rolfe: I note that Dr. Connell refers to small bundles of frog muscles which had been freeze-dried without entirely losing their contractibility. Recent work of Hunt & Matheson[1] has shown that muscle fibres removed from beef steaks dehydrated by the accelerated freeze-drying process also retained their contractility, although contracting to a lesser extent and at a slightly slower rate.

Reference

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CHEMICAL CHANGES IN THE PREPARATION AND STORAGE OF DEHYDRATED FOODS

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Introduction

In such a conference as this, in which some papers deal in detail with individual commodities while others attempt more general surveys of some particular aspects of dehydration, there is inevitably some difficulty in avoiding overlapping. It is proposed in this paper, therefore, to deal primarily with chemical reactions and general principles, stressing the relationships between some of the chemical and physical factors which influence initial quality and keeping properties, and referring to one food or another as necessary to illustrate the point. Much of the discussion will be devoted to browning-type reactions and to lipid oxidations, more particularly in dehydrated animal products.

A basic point which has been mentioned already in previous papers and which needs stressing, is that the material to be dehydrated is, in most cases, a complex chemical or biological system which poses mechanical and physical problems associated with the transference, evaporation and removal of the water, and also those arising from the great variety of chemical and physico-chemical changes (some of which may seriously affect the acceptability of the final product) in and between the constituents of the food.

Loss or production of volatile flavour constituents on drying or heating

One of the most obvious changes in the composition of foods produced by dehydration may be a loss of volatile flavour constituents, which can be serious for commodities which depend to any marked degree on aroma for acceptability. Even for milk there is now evidence that loss of volatile substances, such as traces of lower fatty acids and particularly of methyl sulphide, may be responsible for a lack of 'fresh milk' flavour in the dried product. The threshold concentration for the latter substance in water is said to be as low as one part in one hundred million.[1] Easier identification of the volatile flavour constituents of foods by modern methods of vapour-phase chromatography may make their replacement during reconstitution more feasible.

On the other hand, the direct action of even comparatively slight heat during processing can induce chemical reactions leading to significant changes in flavour, as in the production of 'toffee'-like flavours when butterfat is heated, or when milk powder is stored at high temperatures.[2] Recent American work[3] indicates that the origin of this flavour (termed 'coconut') is due to the production of δ-decalactone from some precursor in the fat. This lactone has now been identified in heated butterfat, milk and cream, and in condensed and dried milk. Compounds of this type have recently been patented as flavouring substances for margarine.

Another example of flavour changes produced by mild heat treatment are those depending on the liberation of labile sulphur compounds in high-protein foods such as milk and egg. It was found that, while spray-dried whole milk retained little or no volatile sulphur, the proteins had been so altered during processing that they liberated volatile sulphur at a lower temperature than did those of fresh milk (Table I).[4]

Table I

Production of volatile sulphur from fresh milk and from milk reconstituted from powder[4]

Milk	Duration of heating, h.	Volatile S produced, mg. per kg. milk solids at	
		60°C	70°C
Fresh	½	0·01	0·08
	1	0·03	0·18
	2	0·05	0·48
	3	0·07	0·76
Reconstituted*	½	0·20	0·35
	1	0·32	0·56
	2	0·51	0·89
	3	0·65	1·22

*From powder spray-dried from milk preheated at 190°F.

The whole subject of flavours in foods is an extremely complex one and instances are continually coming to light where compounds identified as major causes of flavour deterioration in one commodity may be essential or desirable aroma constituents in another.

Enzymic reactions

Logically, it would be reasonable to consider enzymic deteriorative reactions first, but it is not possible to go deeply into this aspect of the subject.

Degradation of labile constituents of tissues is liable to occur as soon as the cells are damaged, and decomposition by tissue (or microbial) enzymes during preparation, drying or subsequent storage is so obvious a potential source of trouble that one of the first criteria for the satisfactory preparation of a stable dehydrated food is frequently the destruction of enzymes, or adequate control of their activity.

With many vegetables a ' blanching ' or ' scalding ' process to destroy, particularly, oxidases is essential prior to dehydration (or freezing) if odour, flavour, texture, colour and ascorbic acid content are to be adequately preserved. Early work establishing these findings has been summarized in the U.K. Progress Reports on Dehydration.[5]

Hydrolysis and oxidation of lipids

In liquid milk, lipase produces undesirable bitter flavours, and the enzyme must therefore be inactivated by pasteurization or pre-heating prior to spray-drying if hydrolytic rancidity is not to develop in the powder during storage. A minor degree of hydrolysis in the fat of manufactured milk products is, however, by no means always undesirable and milk powders with controlled contents of hydrolysed fat have been prepared and used for the manufacture of milk chocolate on a commercial scale, with encouraging results.[6] The effect of lipolysis on the flavour of fats which do not contain fatty acids of low molecular weight is much less marked.

The influence of processing on some of these enzyme systems can be quite complex: milk lipase, for example, is activated by cooling the milk or by homogenizing it.[7] Time temperature inactivation data suggest that more than one enzyme is probably present and, in recent work,[8] one lipase (the ' membrane ' lipase) has been shown to be irreversibly adsorbed on the fat globules as the milk is cooled while another (the ' plasma ' lipase) remains associated with the caseinate.

Little is known of the action of phospholipases in foods although some of them, particularly phospholipase A, are known to be stable enough to withstand ordinary heat processing and drying.

With meat, and particularly with fish, delay in commencing processing can seriously affect the initial quality and keeping properties of the dried product. A marked reduction in the resistance of the fat of meat to oxidation may be produced by the growth of micro-organisms in the tissues before rendering (Table II).[9] Fig. 1 shows more strikingly the adverse effect of storing fresh herring for a few days in ice before drying, on the stability towards oxidation of the oil of the dehydrated product.[10] In this case haem-protein catalysis rather than a true enzymic action is probably responsible.

Fruit and vegetables usually contain very little lipid. Lee[11] gives values for the total crude lipid content of asparagus as 0·15–0·3; maize 0·75–0·84; lima beans 0·33–0·49; peas 0·34–0·48; snap beans 0·09–0·14 and spinach 0·27–0·58 %. Potatoes have been found to contain less than 0·2 % of fat, containing 28 % of linolenic and 41 % of linoleic acids.[12] Despite these very low lipid contents, recent work suggests that lipid oxidation may play an important part in the

Table II

Effect of delay in rendering on the resistance of rendered beef fat to oxidation[9]

Condition of crude fat	Rendered fat	
	Free acidity (as % oleic acid)	Induction period, h. at 70°C
Freshly killed	0·10	150
Held 3 days in a moist atmosphere	2·61	3–15

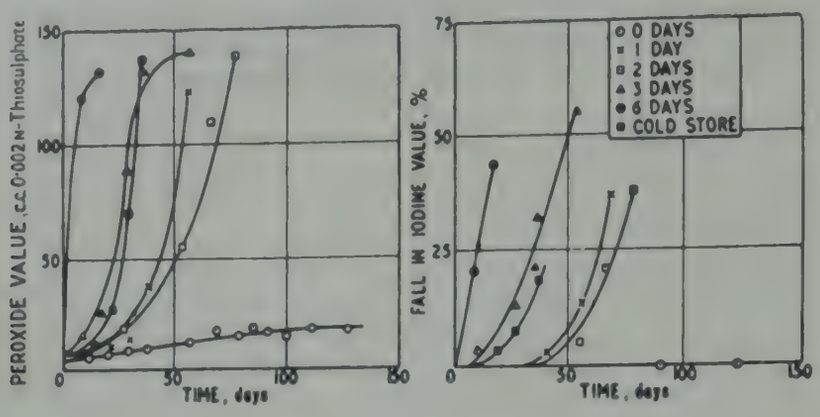

FIG. 1. *Effect of storage of the fresh herrings for 0–6 days in ice, or for 2½ months at —30°, on the stability of the dehydrated fish at 10° (ref. 10)*

development of ' hay-like ' off flavours in dehydrated and frozen vegetables, while coupled oxidations of carotenoids, chlorophyll and ascorbic acid can be responsible for loss of colour and vitamin activity. Dried grass or lucerne is another commodity in which serious oxidative deterioration of this type can occur, with consequent reduction in its valuable pro-vitamin A content.

The participation of an enzyme or heat-labile catalyst system in these changes is shown by the powerful stabilizing effect of blanching. In recent work[13] unblanched peas, sweet corn and snap beans have been found to develop ' off ' flavours in frozen storage after as little as 2–4 weeks at 0°F. The crude lipid extracts showed a marked increase in free acidity after the vegetables had been stored for one week and positive tests for peroxides were obtained after 3 weeks (peas), 1 month (beans) and 2 months (maize). ' Off ' flavours in blanched maize developed only after 12 months and peroxides were present after 18 months. Enzymes which are still able to function at the low temperatures and activities of water obtaining in the frozen state would be likely to remain active also in dehydrated products.

In most cases the enzymes or catalysts involved in these oxidative changes have not been adequately characterized. Mapson & Moustafa[14] showed that the pea contains both cyanide-insensitive (true lipoxidase) and cyanide-sensitive lipid- and glutathione-oxidizing systems. The lipid substrate in extracts of the ungerminated seeds was not readily available to the enzyme but became so on germination of the seed or on treatment of extracts of the ungerminated seeds with small amounts of certain alcohols. Siddiqi & Tappel[15] have confirmed the presence of a true lipoxidase in the pea, as well as in lucerne[16] and in a recent paper[17] they give the relative activities of the enzyme in several plant seeds as soya-bean 100, pea 35, wheat 2 and groundnut 1.

Enzymic browning

Many fruits and vegetables undergo rapid deterioration following mechanical or physiological damage during processing. Prominent among such changes is ' enzymic browning,' in which natural pigments present may be destroyed or masked by a reddish or dark brown discoloration, while odour and flavour are adversely affected and readily oxidizable nutrients such as ascorbic acid and carotene are destroyed.

Enzymic browning is due to the oxidation of phenolic substances, particularly *o*-diphenolic compounds such as *epi*catechin and the chlorogenic acids, by atmospheric oxygen under the influence of polyphenolase enzymes. The phenols are oxidized to *o*-quinones which then undergo further oxidation and polymerization to dark compounds of the type which will be considered further in connexion with non-enzymic browning.

Control can, in some cases, be exercised by selection of the variety and stage of maturity of the material to be processed to be as deficient as possible in substrate or enzyme, as well as by physical means such as heating to destroy the enzyme or exclusion of oxygen. Ascorbic acid (or its cheaper, synthetic isomer D-*iso*ascorbic acid) inhibits the reaction, probably in part by absorbing free oxygen, but also in part at least by reducing back the quinonoid oxidation product to the parent phenol.[18] Sulphur dioxide apparently functions both as a chemical

reducing agent and inhibitor of browning, and as a deactivator of the enzyme. Lowering the pH by the addition of citric acid is beneficial in some cases, delaying browning by reducing the activity of the enzyme and by complexing trace metals, thereby permitting adequate stabilization with lower concentrations of ascorbic acid. Sulphydryl-containing compounds such as cysteine, or thioamides such as thiourea or phenylthiourea,[18] also show protective action, possibly owing to their copper-deactivating properties, but thiourea, which has been used for this purpose, is now known to be carcinogenic.

Non-enzymic browning

Perhaps the commonest and most important type of chemical change which can occur in concentrated and dried foods, in which microbial and enzymic changes have been largely inhibited, is non-enzymic browning. Much has been written on this subject and it will only be possible here to touch upon a few of its aspects.

Symptoms of non-enzymic browning

Deleterious changes associated with reactions of the browning type vary considerably from one food to another and may include any of the following: development of a brown discoloration ranging from a pale cream or biscuit shade to almost black; production of stale, caramelized, bitter or otherwise unpleasant odours or flavours; loss of solubility of the protein leading to deterioration in texture and to a failure of dried foods to reconstitute properly with water; a reduction of pH and the production of carbon dioxide and water; enhanced reducing properties leading to interference with the estimation of ascorbic acid with 2:6-dichlorophenol-indophenol and of reducing sugars by the cuprimetric and ferricyanide methods; an increased tendency to froth or foam; the development of the property of fluorescing in ultra-violet light; and finally, a loss of nutritive value of the protein resulting from a reduced availability of certain of the essential amino-acids, and a destruction of ascorbic acid when present.

Conditions under which deteriorative browning develops

Trouble attributable to non-enzymic browning is liable to develop either rapidly during the pre-cooking or drying process itself or, more slowly, during storage of the dried product prior to consumption. A certain amount of moisture is essential for most browning reactions and drying to a sufficiently low moisture content is a usual method of control: on the other hand, a dried product allowed to equilibrate with a moist atmosphere offers nearly optimal conditions for deterioration of this type. The temperature coefficients of the chemical reactions concerned are high, and trouble may therefore be experienced in the tropics with materials which store reasonably satisfactorily in temperate climates; conversely, browning is rarely, if ever, troublesome under chilled or frozen conditions of storage. Atmospheric oxygen is usually not essential for discoloration and may even decrease the extent of browning: in other cases browning is greatly accentuated in the presence of oxygen and other consequences of the reaction such as the nature of the 'off' flavour produced and the amount of carbon dioxide evolved can be markedly affected.

Nature of the constituents of foods concerned in browning

Most of the carbohydrate constituents of foods will form brown caramelization products by a complicated process of dehydration and polymerization if heated sufficiently strongly, reducing sugars such as arabinose, xylose, glucose and fructose decomposing more rapidly than sucrose and starch, and glucuronic, galacturonic, ascorbic and reductic acids more easily still. These reactions can be accelerated by alkali or acid, and particularly by amino-compounds, and then proceed extensively at much lower temperatures. In some foods, such as molasses, honey or maple syrup the amount of non-carbohydrate materials involved may be so small that the browning reaction appears to be little more than a catalyzed caramelization of sugar. In fruits and vegetables, organic acids, including ascorbic, can take part in complicated interactions with reducing sugars and amino-acids, while in protein-rich foods such as fish and egg-white, comparatively minor proportions of sugars are able to produce serious changes in the proteins which constitute the major part of the food.

In addition to proteins and amino-acids, other nitrogenous food constituents such as the B-vitamins, thiamine, nicotinamide and *p*-aminobenzoic acid, can also undergo reactions of

the browning type with reducing sugar, and this is probably one of the routes by which losses occur during the processing and storage of preserved foods.[19]

Finally, in dried egg yolk, traces of glucose are known to react with the lipid amino-groups of kephalin, with a resulting serious deterioration in palatability and colour.

Browning in individual foods and in model systems

Dried egg

Interest in the browning reaction in high-protein foods arose from work on dried egg during the war, when much effort, both in this country and in the U.S., was devoted to elucidating the nature of the chemical reactions responsible for the serious deterioration in colour, flavour, texture and aerating properties which occurred during the dehydration and subsequent storage of the product. Dried egg white, which contains about 83% of protein and 3% of glucose, becomes brown and insoluble on storage and develops a water-soluble fluorescence, changes which have been traced to the occurrence of a Maillard-type reaction between the proteins and the glucose. A similar protein–sugar interaction undoubtedly also occurs in the yolk, but, in addition, American workers have shown that another amino–aldehyde reaction between the glucose and the free amino groups of the kephalin fraction of the phospholipid also occurs. This latter reaction, which appears to be largely responsible for the 'off' flavours produced, results also in an increased absorption in the ultra-violet and a visible darkening of the phospholipid fraction of the yolk, as well as in the development of an ether-soluble as distinct from a water-soluble fluorescence.

Since the war, several procedures have been developed for delaying or preventing this sugar-induced deterioration in dried egg. In one process adopted by the U.S. Quartermaster Corps,[20] browning reactions were delayed by acidifying the pulp with HCl to pH 5·5 before drying to a low moisture content, sufficient $NaHCO_3$ being added to the powder to restore the pH, on reconstitution and cooking, to a value of 7·5–7·8.

More recently, further improvements in the keeping properties of dried egg products at high storage temperatures have been achieved by fermenting away the glucose prior to drying, either with yeast [21–25] or with glucose oxidase and catalase in the presence of H_2O_2,[26] the powder in either case being dried to a moisture content below 2·3%.

Acidification before drying apparently reduces the glucose-induced phospholipid and protein deteriorations to one-third or less of that in the untreated powder, as shown by chemical methods, but is not so effective as removing the glucose entirely.[27] Palatability tests showed a similar preference for the glucose-free powders,[28] and differences in colour and texture were even more marked. It was concluded that the shelf life of glucose-free dried egg at 2% moisture content should exceed 18 months at 100°F. All of these storage tests were, of course, carried out in inert gas, to prevent oxidative deterioration of the lipids.

A major defect of commercial spray-dried egg for cake-making as compared with the fresh or frozen product, is its inferior aerating power. Much of this loss of aerating power can be prevented by the addition of a high concentration of sucrose (15% of the pulp) to the liquid egg before drying.[29] Sucrose has also been observed to protect the isolated lipoprotein of egg yolk from denaturation during freezing or freeze-drying, and during subsequent storage in the dried state,[30] and to delay greatly the onset of glucose-induced insolubility in freeze-dried milk protein.[31]

Dried skim milk

Milk is another interesting system from the viewpoint of browning reactions, since the major constituents of its non-fat solids are lactose and protein in the ratio of approximately 3 : 2 by weight, and symptoms of a browning reaction (although not necessarily a marked discoloration) are liable to develop during the preparation and storage of both dried and condensed milks, as well as in heat-sterilized fresh milk.[32]

In a study of the protein–sugar reactions in dried skim milk a stoicheiometric reaction was demonstrated between the free amino-groups of the protein, which are mainly the ε-amino groups of the lysine residues, and the lactose (Fig. 2, A & B).[33] During the early stages of the reaction, protein and sugar combined without appreciable loss of solubility or increase in

colour (Fig. 2, C, D & E), insolubility and discoloration developing subsequently by decomposition of the first-formed complex.

The protein–sugar intereaction in skim milk powder increased rapidly at moisture contents above about 5%, and at a storage temperature of 100°F there was also a rapid loss in nutritive value, mainly as a result of the lysine being rendered unavailable by reaction of its ε-amino groups with the lactose.[34] At lower moisture contents and storage temperatures no appreciable loss of biological value of the protein occurred and, under all conditions of storage, a serious reduction in palatability preceded loss of nutritive value of the protein.[35] Regier & Tappel[36] have similarly found that freeze-dried beef which had deteriorated by browning reactions until organoleptically unacceptable showed no loss in nutritive value of the protein for chicks.

An interesting feature of the work on milk powder was the excellent correlation observed in the early stages of deterioration between the capacity of the milk to reduce potassium ferricyanide and the primary reaction between the protein amino-groups and the sugar (Fig. 2, F).

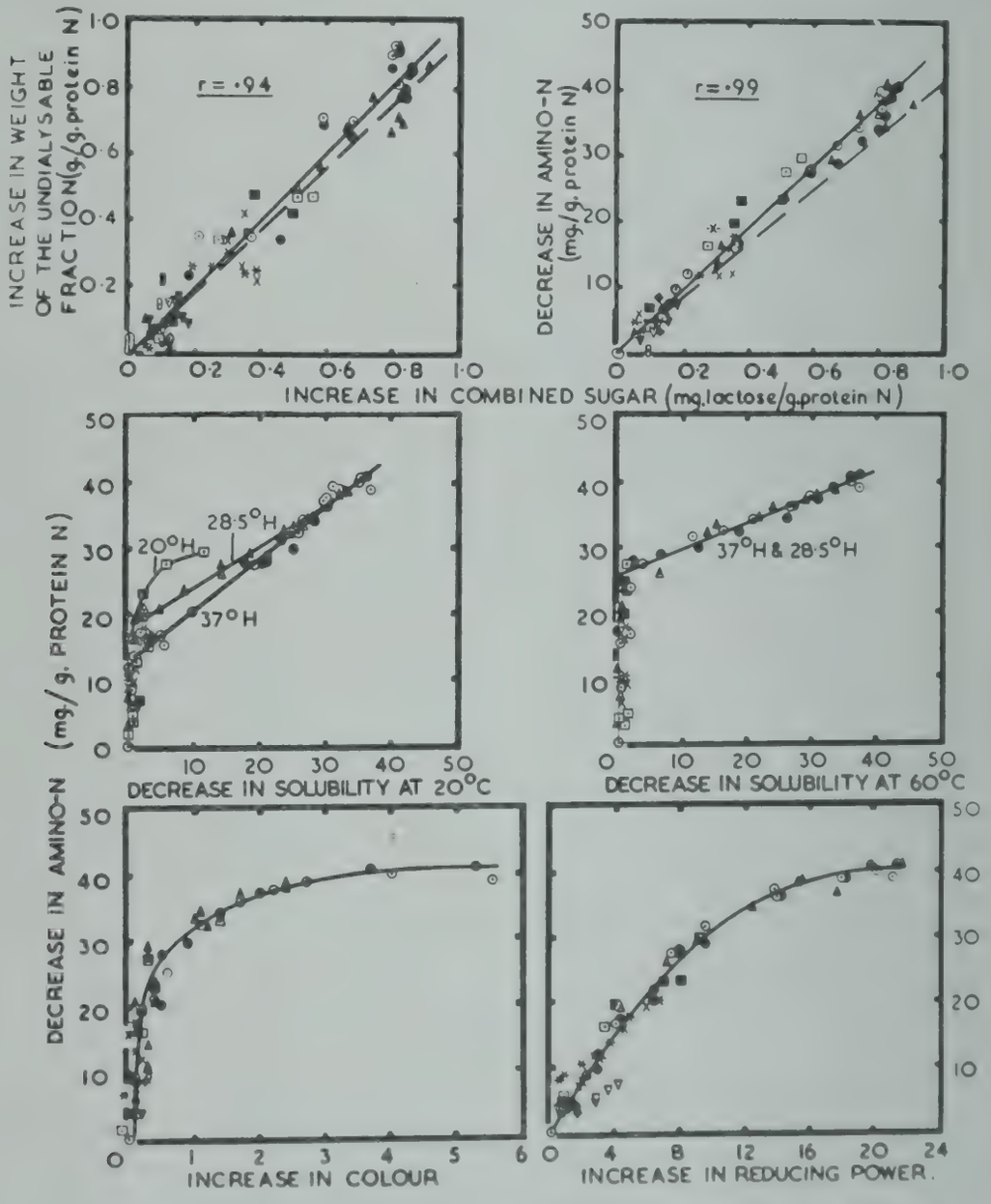

FIG. 2. *Inter-relations between various chemical and physical changes in stored skim milk powder*[33]

The symbols used denote different conditions of storage. Three powders of 7·3 (H), 4·7 (M) and 2·9% (L) moisture content were stored at 37, 28·5 and 20°, in air or in nitrogen (solid symbols) for periods ranging from a few days up to 2 years. The most rapid changes were shown by H powder at the three temperatures (O, ▲, □) and by M powder at 37°(×).

This ferricyanide-reducing test had originally been introduced as a measure of denaturation of the protein, with liberation of —SH groups, but was subsequently shown to be due essentially to the protein–sugar reaction.[37]

In a modified version of the test, in which the reaction is carried out on the milk protein after precipitation with acid and re-solution in urea instead of on the powder itself,[38] the ferricyanide-reducing test seems to show promise as a simple means of following the progress of protein–lactose interaction during the precondensing and drying of milk. Kumetat & Beeby, in a recent paper,[39] have shown that increases in reducing power during precondensation are greater the higher the temperature and the greater the concentration of milk solids. Values found for the concentrate in six commercial plants ranged from 0·9 to 3·6 mg. ferricyanide/g. protein, according to the operating temperature and type of evaporator. Further increases in reducing power (to 2·9–12·3) occurred during spray-drying, and were greatest where the powder remained in the hot chambers for a considerable period. Powders with very high reducing values (8·9, 11·3) were also obtained from a dryer of high thermal efficiency in which the feed milk was used to scrub out the entrained milks solids from the exit gases, so that some of the milk was recirculated through the dryer, perhaps several times.

Because of the incipient protein–sugar interaction which normally occurs during precondensation and drying, the ferricyanide-reducing power can be used to detect the 'extension' of liquid milk supplies with reconstituted spray skim milk powder, a practice which has now assumed considerable importance in some countries. In a recent American survey[40,41] values for raw fresh milk from widely scattered areas ranged from 0·90–4·18, average 2·28 mg. ferricyanide 100 ml. Ordinary pasteurization caused very little increase, but 37 'low heat' and 16 'high heat' commercial spray skim powders ranged from 6 to 40 and from 12 to 60 mg./100 ml. (reconstituted basis) respectively.

The occurrence of the first stages of browning reactions in milk powder during manufacture is of particular interest at the present time in connexion with recently introduced processes for increasing the reconstitutability of spray-dried skim milk ('Instantizing'). These depend on damping the powder with steam (which causes clumping of the particles into large, loose aggregates, and partial crystallization of the lactose), followed by re-drying. Such procedures are carried out under conditions likely to favour protein–sugar interaction, and therefore require careful control if adverse effects on flavour and subsequent keeping properties are to be avoided. Preliminary data along these lines have already been published.[42]

Protein–sugar systems

For a study of model protein–sugar systems the technique was introduced of freeze-drying a solution containing the protein and the sugar, after adjustment to the required pH, the required range of low moisture contents being maintained during storage by controlling the atmospheric humidity.

Under these conditions the reaction between the protein amino groups of casein[43] or insulin[44] and glucose was very slow in aqueous solution and virtually zero in the completely dry solid, but proceeded at a maximum rate at a moisture content corresponding to a R.H. of 65–70% (Fig. 3). This optimum R.H. was not the same for all systems, being appreciably lower

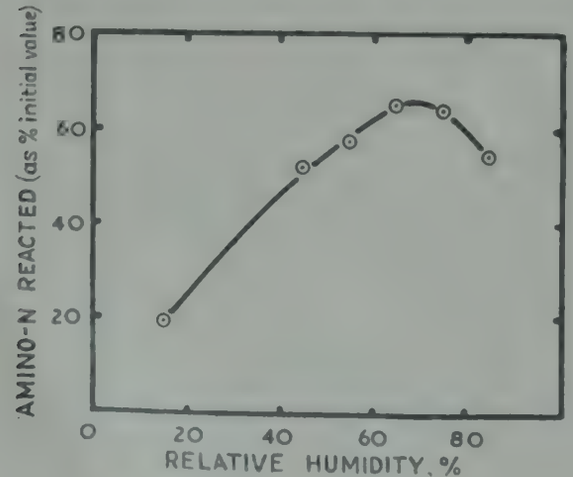

FIG. 3. *Influence of humidity on the rate of reaction of insulin with glucose*

(Insulin reacted with 1·5 equivalents of glucose per amino-group for 16 days at 37°) (ref. 45)

(55% R.H.) in blood plasma–glucose,[45] and lower still in model systems of α-*N*-acetyl-lysine or polylysine, [46] which contained a relatively much higher content of free amino groups than normal proteins and therefore required a correspondingly larger proportion of the hygroscopic, glassy sugar for stoicheiometric reaction.

From casein, a casein–glucose complex was prepared which had lost 70% of its original free amino groups and contained 7% of firmly bound glucose, but which was still fully soluble and practically colourless. On further storage at 37°C it browned and became insoluble.[47] A considerable proportion of the bound lysine could be recovered from the colourless intermediate product on acid hydrolysis, but none of the glucose.[48] The resistance of the amino acid–sugar linkage to digestive enzymes was shown by the rapid fall in the biological value of the casein on reaction with glucose (Table III).[49]

Table III

Changes in the nutritive value of casein stored with glucose under nitrogen at pH 6·3, 70% R.H. and 37°C[49]

Length of storage, days	Biological value		Protein efficiency	
	Mean value for 12 rats	Standard error	Mean value for 12 rats	Standard error
0	77·9	± 1·38	2·42	± 0·300
5	61·6	± 1·11	1·95	± 0·103
30	38·7	± 1·00	0·32*	—

*Two rats lost weight

As the duration of storage increased, the ratio of glucose to amino-N reacted, in an initially 4 : 1 (molecular) mixture, increased from approximately 1 : 1 at 5 days to 2 : 1 after 1 month and 3 : 1 after 3 months' storage,[47] and amino-acids other than lysine became increasingly involved.[50]

The optimum R.H. for browning and for loss of solubility was usually higher than for the primary amino-acid–sugar condensation,[47] and the rate of the reaction increased markedly with increasing pH (Fig. 4).[51] The temperature coefficient was always high (Q_{10} 15–25° = 5·4)[44] and, as had been found for amino-acid–sugar systems, pentoses were considerably more reactive than hexoses.[52]

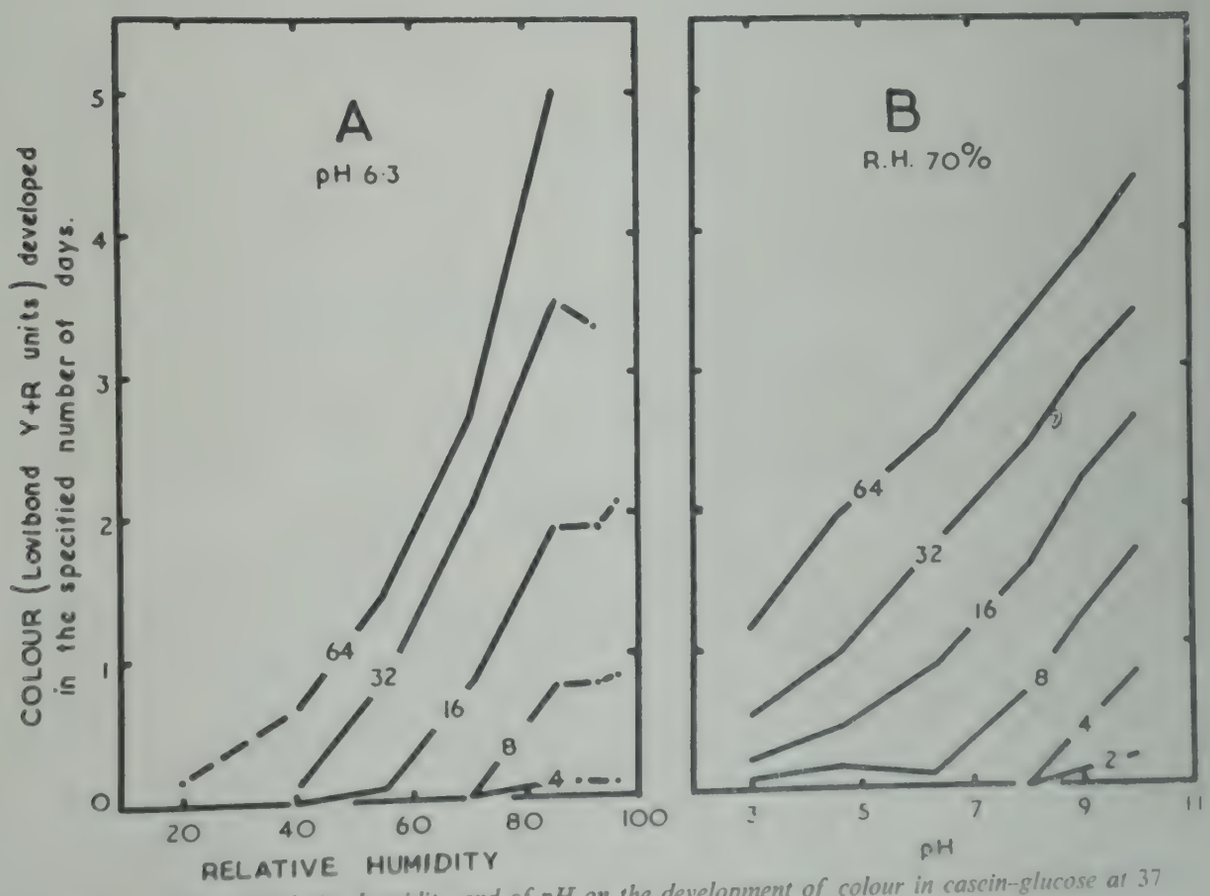

FIG. 4. *Effect of relative humidity and of pH on the development of colour in casein–glucose at* 37 (*ref.* 51)

Meat and fish

Much of the interest in the non-enzymic browning of meat and fish has centred on the water-soluble 'extractives' which contain amino-acids, peptides and other nitrogenous substances in addition to small quantities of reducing sugars. Browning phenomena in dehydrated meat are being discussed later by Sharp & Rolfe (see p. 197).

In fish, Tarr has stressed the importance of Maillard-type interactions between the various amino-containing constituents of the muscle and reducing sugars, particularly ribose, in producing browning during autoclaving.

Jones,[52a] studying the browning of freeze-dried extractives of fish muscle at 60°, observed maximum browning at about 30% R.H., with the usual high temperature coefficient. The rate of discoloration increased with pH up to 7, but thereafter decreased owing to a loss of reactive volatile amines from the system at higher pH levels.

In dehydrated homogenate of whole codling muscle browning did not show any obvious maximum with change in water content, but increased over the range 0-90% R.H. (cf. Fig. 4). In freeze-dried dialysed homogenate, which alone failed to brown, the addition of methylhistidine (formed in the muscle, post mortem, by the enzymic splitting of anserine) caused a rapid browning of the exposed surface when exposed to daylight at 15°, even in the complete absence of water. Under moist conditions a yellow discoloration developed throughout, in the absence of light, and increased rapidly in intensity with increasing temperature. Since the dialysed muscle preparation contained no free sugar and developed none during storage these data show that sugar–amine reactions are not the only factors capable of producing discoloration in dehydrated fish during storage, but that the spontaneous degradation of ring compounds such as methylhistidine may also be important.

Amino-acid–sugar reactions

Despite the apparently greater simplicity of the amino-acid–sugar system, little progress had been made in the earlier work in isolating intermediate products, probably because of the extreme complexity of the reaction in aqueous solution under alkaline conditions or at high temperatures, where secondary browning and polymerization follow rapidly on the primary condensation. Gottschalk & Partridge,[53] however, reacting lysine or alanine with glucose at pH 8·5, 70% R.H. and 37°, and Hannan & Lea,[46] reacting α-*N*-acetyl-lysine with glucose at pH 6·3, 20-60% R.H. and 37°, were able chromatographically to separate colourless intermediate reaction products, which gave colour reactions for both an amino-acid and a sugar and which yielded typical browned and fluorescent substances on further storage or on heating. At a low R.H. (20%) the intermediate was obtained with practically no secondary decomposition, but browning increased as the R.H. was raised.[46]

The properties of these colourless intermediate products suggested that they were *N*-substituted 1-amino-1-deoxy-ketoses (or their enolic forms) produced by an Amadori rearrangement of the *N*-glycosides or Schiff bases formed as first products of the condensation of the amino-acid and glucose (Fig. 5).

Richards' recent study[54] of the chemical properties and infra-red spectrum of the intermediate compound from the glycine–glucose reaction at pH 6·7, 70% R.H. and 37° suggests that the product exists almost entirely in the enolic form.

Gottschalk & Partridge[53] observed that the reactivity at pH 8 and 70% R.H. of an amino-group in an amino-acid increased with its distance from the carboxyl group, the α-amino-group of lysine being very much less reactive than the ε-group. Willits *et al.*[55] similarly found that lysine was the only amino-acid to cause even slight browning at pH below 7 when heated with glucose in dilute solution, an alkaline pH being essential for the others. German workers[56] have shown that synthetic *N*-glycosides are readily hydrolysed in acid, neutral or basic solvents, only those of lysine (and ornithine) being sufficiently stable to be detectable on chromatograms. On the other hand, Folk,[57] using a fluorodinitrobenzene technique, has found the α- and ε-amino-groups of lysine to be of approximately equal activity in aqueous solution at pH 8·5.

In earlier work, Schwartz & Lea[44] had shown that the terminal α-amino groups of insulin react with glucose (at pH 7 and 65% R.H.) at least as rapidly as the ε-amino groups of the lysine side-chains, and evidence had been produced of other reactions requiring an alkaline pH

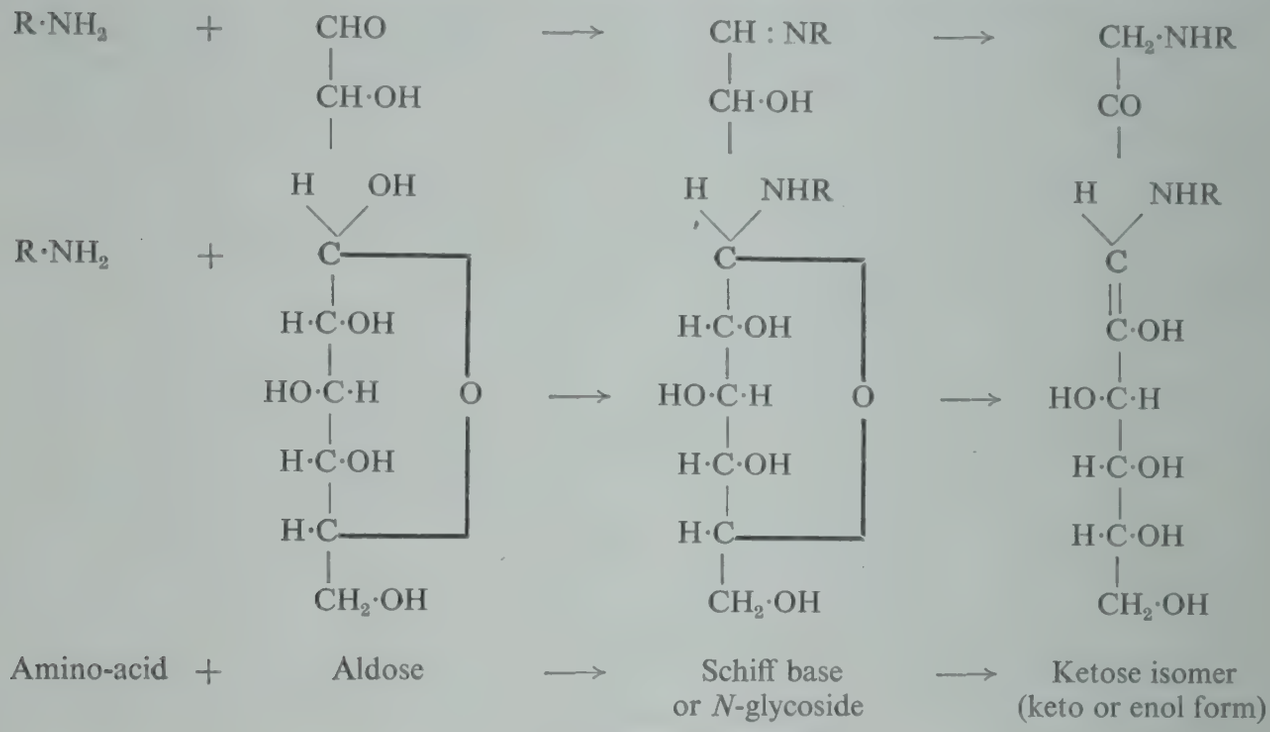

FIG. 5. *The Amadori arrangement*

in aqueous solution which proceeded in the presence of protein dried to an equilibrium R.H. of 70% from an aqueous solution at pH 6·3.[58]

Haugard & Tumerman[59] point out that α-amino-groups in peptides and proteins have lower p*K* values than those of amino-acids and might therefore be expected to react under more acid conditions. They have used an ingenious solubility method to demonstrate at pH values as low as 5·4 the initial reversible combination of β-lactoglobulin and glucose to form the *N*-glycoside or Schiff's base, followed by its secondary, irreversible decomposition. The type of curve obtained, from which constants for the two phases of the reaction can be calculated, is shown in Fig. 6.

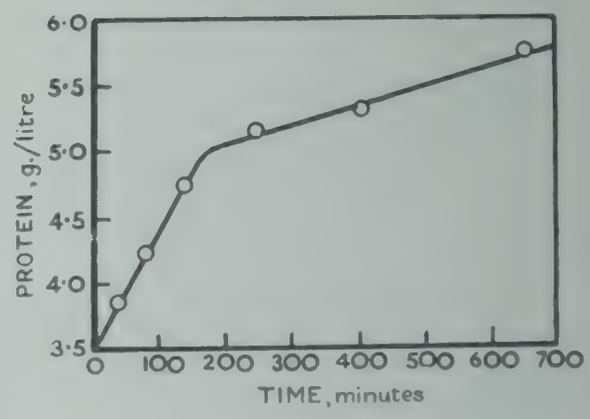

FIG. 6. *Reaction of β-lactoglobulin (saturated solution) with molar glucose at 23·9°. pH maintained at 5·4*[59]

Fruits and vegetables

Wager,[60] applying chromatographic and ion-exchange methods to a study of browning reactions in dehydrated carrot and potato, concluded that a Maillard-type of reaction is the first and most important cause of browning in these vegetables. From carrot he obtained a colourless intermediate product of similar properties and probable structure to those which had been isolated from amino-acid–sugar systems.

In very recent work, Australian investigators[61,62] have synthesised Amadori-rearranged products from the condensation of glucose with a range of amino-acids, and have determined their order of displacement on ion-exchange columns. Compounds from the reaction of glucose with glycine or β-alanine, and of fructose or xylose with glycine were obtained pure and crystalline.

They then examined browned, freeze-dried apricot and peach purees, which had been stored for 4–16 months at 25°C, and 70% R.H., by extraction with 80% ethanol and fractionation of the extracts by ion exchange and paper chromatography. In addition to the amino-acids, organic acids, sugars and polyhydroxy compounds present in the fresh products, the stored samples also contained eleven Amadori products derived from glucose and two from fructose, together with nine by-products of unknown composition derived from aspartic acid or asparagine and glucose, and three from ammonia and glucose. Some sugar mono-esters of malic and citric acid were also present.

Although amino-acids, particularly lysine and glutamic acid,[63] may make some contribution to the browning even of citrus juices, reactive carbohydrates such as ascorbic and reductic acids, when present in sufficient quantity, can themselves produce the usual symptoms of browning quite independently of amino-acids.[64] Since the reactive intermediate in these cases is the dehydro-acid, ascorbic-acid-induced browning is greatly enhanced by atmospheric oxygen, whereas in protein–sugar,[33] amino-acid–sugar[65] or kephalin–sugar[66] reactions discoloration may be independent of, or even decreased by, access of oxygen. According to a recent report, ascorbic acid, according to its concentration, can either inhibit or promote browning.[67]

In common with browning in animal products, this form of spoilage in fruits and vegetables shows the characteristic marked dependence on moisture content and high temperature coefficient:[68,69] Gooding & Duckworth[70] have recently demonstrated that changes in the culinary properties, colour, flavour and texture of dehydrated vegetables occurring during storage for one month at 37°C can be reproduced in one day at 55°C.

The mechanism of browning

The foregoing brief survey shows that considerable progress has now been made in elucidating the mechanism of the earlier stages of the amino–sugar reaction and of the factors influencing it, but that much still remains to be learned about the mechanism of the subsequent changes whereby the Amadori-rearranged products are converted to the brown substances themselves.

The complexity of this problem is well shown in a review by Hodge,[71] which sets out diagrammatically the inter-relationships between a number of reactions probably involved in the production of ' melanoidins ' from amino–sugar systems. According to this scheme, either dehydration to the Schiff's base of hydroxymethylfurfural (as suggested by Gottschalk & Partridge[53]) or reductones, or fragmentation of the sugar residue, or Strecker degradation of the amino-acid residue occurs, the reactive intermediates then polymerizing to unsaturated, fluorescent, coloured polymers. The chief reactions involved are considered to be aldol condensation, aldehyde–amine condensation and the formation of heterocyclic nitrogen compounds. Hurd & Buess,[72] on the basis of studies with simple model systems, particularly stress the importance of aldolization and/or oxidation mechanisms as fundamental processes in the browning of the sugars, with the production of polymers containing cumulative carbonyl groups.

The control of browning reactions

The most generally applicable means for controlling browning reactions in dehydrated foods are drying to sufficiently low moisture contents (with or without the aid of in-can desiccants), maintaining these low moisture contents during storage, and avoiding exposure to high storage temperatures. Special means applicable in particular cases include selection for drying of raw materials of low content of reactive browning substances, and storage prior to drying under conditions calculated to prevent the accumulation of browning reactants. Low contents of basic amino-acids and of reducing sugars (particularly pentoses) in potatoes, for example, have been shown to be associated with light colour in potato chips:[73] the pronounced effect of the time/temperature conditions under which meat is held prior to drying on its content of reducing sugars and consequently on the browning of the dehydrated product is described by Sharp & Rolfe.[74] Special pre-dehydration treatment, by extraction or fermentation, may be used to remove one or more of the reactants, usually a minor constituent (e.g., in egg). Benefit may sometimes be obtainable by alteration of the pH, with return to normal if necessary on reconstitution (e.g., for egg). In compounded foods it may be possible to segregate a reactive constituent by encapsulating, enrobing or other means. The only chemical inhibitor of browning

widely used in dehydrated foods is sulphur dioxide, in dried fruits and vegetables. Sulphite apparently does not interfere with the early stages of the amino–sugar reaction, but probably blocks subsequent browning by inactivating traces of reactive carbonylic substances which function as intermediates in the degradation of the sugars.

Lipid oxidations

Virtually all foods which are dehydrated contain lipids, ranging from the small amount present in most fruits and vegetables to major proportions in most animal products. Removal of the water, frequently the largest constituent of the food by weight, tends to leave the residue in a sponge-like condition in which access of oxygen to the interior is greatly facilitated. Whether or not oxidation of the exposed lipid will be likely to cause trouble during dehydration or subsequent storage will be the resultant of the action of a number of factors, some for and some against.

Autoxidation of a fat or phospholipid can be considered as consisting essentially of combination of the unsaturated fatty acids with oxygen to produce mainly hydroperoxides, which then react further by dehydration, fission, polymerization or further oxidation, to yield a variety of degradation products, including the volatile aldehydes, ketones and acids which are largely responsible for the objectionable odours and flavours.

But it is not only the oxidation of the fats themselves which causes deterioration; other constituents of foods are oxidizable too, and tend to be destroyed when the fat oxidizes. Probably they are largely destroyed by reaction with the free radicals produced during the chain oxidation of the fats. Pigments, flavour constituents and vitamins are only minor components of food on a weight basis, but they are very important in determining appearance, palatability and nutritive value, and damage to them can easily make a food unacceptable.

Deterioration by reaction with atmospheric oxygen is not confined to foods of high fat content, witness the ' violet ' odour resulting from the oxidation of carotene to β-ionone which so soon terminates the shelf life of air-stored dehydrated carrot.[68] Even with mashed potato powder, changes associated with lipid oxidation can be limiting at low moisture contents,[75] and they probably occur also in skim milk powders under similar conditions.[33] With products of high fat content, such as dehydrated pork or whole milk powder, obvious tallowy flavours usually develop fairly rapidly unless adequate precautions are taken to exclude oxygen or otherwise to control its reaction with the fat.

Factors which influence the oxidation of lipids

Factors which tend to accelerate the oxidation of lipids include a high degree of unsaturation; exposure to high temperature, or to ultra-violet or blue light, or to ionizing radiations; contamination with peroxides, such as those of oxidizing fats, or with trace metals, particularly copper or iron; or the presence in the system of lipoxidase enzymes, or of haem-protein catalysts, such as haemoglobin or cytochrome *c*. Possible methods of control therefore include:

(1) Limitation of access of oxygen, whether by tight packing, minimization of headspace in containers, gas-tight sealing or inert gas- or vacuum-packing. A recent development in this direction is the enrobing of readily oxidizable materials, such as vitamin A or flavouring substances, in hardened fat, wax, gelatin or starch, with the object of excluding oxygen or of preventing contact with pro-oxidant constituents in a mix. In some cases an oxygen scavenger such as palladium and hydrogen[76] may prove useful for removing the residual free oxygen in a sealed container.

Reducing the available oxygen within practically obtainable limits usually largely eliminates oxidative spoilage. With spray-dried whole milk powder, for example, optimal keeping properties are obtained in the presence of not more than 0·01 ml. of oxygen g. of powder (corresponding to approximately 1% oxygen in the head-space gas, after ' desorption '), with slightly reduced but still useful protection obtainable at two or three times this level.[2] With pre-cooked, air-dried meat, compression to a density of 1 g./c.c. in a gas-tight container, without inert gas- or vacuum-packing, has been found to give adequate protection against rancidity.[76]

(2) Low storage temperatures will reduce the rate of oxidation, although, when catalysts such as lipoxidase or haemoglobin are active, the protective effect of low temperatures may be unusually small.

(3) Access of ultra-violet or visible light can be prevented by the use of opaque or coloured wrappers or containers.

(4) Contamination by pro-oxidants, particularly copper, iron or oxidized fat, can be avoided, and no opportunity given in the pre-drying period for the growth of oxidase-producing micro-organisms. When practicable, admixture with salt can be avoided in those products in which it is found to have a de-stabilizing effect. ' Blanching ' or other heat treatment may be used where heat-labile pro-oxidant systems such as lipoxidase are operative.

(5) Control of the moisture content of ' dry ' products at not too low a figure is often beneficial, because rancidity decreases and deteriorative browning reactions increase with increasing moisture content. When oxidation is prevented by exclusion of oxygen the moisture content can be reduced further to prevent browning.

(6) Natural antioxidants, such as the tocopherols, should be preserved as carefully as possible during processing. They can sometimes be reinforced by the incorporation of edible stabilizing material, such as spices, sugar, citric acid, soya or cereal flour, or by smoking, or by the production of antioxidant-active material in the food itself by heating.

(7) Within the limitations imposed by the ' Antioxidants in Foods Regulations ' non-toxic chemical oxidation inhibitors may be used.

The application of these principles to the preparation and storage of dehydrated foods is not always simple. While it is true, for example, that oxidation during vacuum-drying is likely to be less than during air-drying, and that storage in gas-tight containers *in vacuo* or in inert gas is widely and successfully used for minimizing oxidative deterioration, it does not follow that no flavour problems of an oxidative type can ever arise under these conditions.

Sealed containers of stored dehydrated foods from which oxygen has been largely excluded can sometimes show ' off ' odours, e.g., ' fishy ' or ' crab-like ' in dried meat, ' fruity ' in dried milk or ' muttony ' in hydrogenated lard, which are not present in the air-stored material. The origin of such odours, which may disappear on cooking or even on exposure to the air, is usually not known with any certainty, but they may be due to unstable partial oxidation products which do not accumulate with free access of oxygen. Of somewhat similar origin, and perhaps related to the ' reversion ' phenomena shown at very low levels of oxidation, particularly by fats containing polyunsaturated fatty acids, may be the ' fishy ' flavours observed by Ratcliff & Brooks[77] to develop in stored, dried ox-blood plasma. This phenomenon showed some of the characteristics of air oxidation, in that it appeared to be promoted by haemoglobin, but no ordinary standard of gas-packing sufficed to prevent it. It seems possible that the phospholipids and or sterol esters of the blood lipids may have been involved. ' Fishy ' off flavours in oxidizing dairy products are sometimes observed to pass to tallowy flavours on further storage.

A case of unusually rapid oxidation of the fat in an air-stored dehydrated product was that of the cured meats prepared by Bate-Smith *et al.*,[78] in which the combined action of the curing salts and the muscle pigments apparently produced a catalyst which was extremely potent in the dried material.

Inter-relations between lipid oxidations and browning reactions

Browning reactions characteristically set up powerful reducing conditions, as shown by the reduction of reagents such as 2 : 6-dichlorophenolindophenol and ferricyanide, whereas the autoxidation of fat entails the production of hydroperoxide radicals of high oxidizing potential. Which of the two forms of spoilage takes precedence may well be decided by factors such as moisture content and storage temperature, high moisture and temperature favouring browning and low moisture and temperature favouring rancidity (Table IV).[79] The optimal moisture content for a dried product may, therefore, be higher in the presence of air than when oxygen is effectively excluded and rancidity prevented by inert-gas packing.

Several demonstrations of the antioxidant activity of products of browning reactions have been made recently. German workers[80-82] showed that the ' melanoidins ' produced by heating glucose and glycine together in concentrated solution showed a useful stabilizing effect on the fat of biscuits: the same effect could be produced by adding the glucose and the glycine themselves to the mix before baking. American work[83] confirmed the antioxidant action of glycine–glucose reaction mixtures, and showed that aqueous extracts of sweet biscuits possessed increased antioxidant properties for fats when a small proportion of the sucrose in the mix

Table IV

Effect of moisture content on the type of deterioration predominating in (air-packed) spray-dried whole milk[79]

Moisture content	Colour (Weeks at 37°C)				Flavour (Weeks at 37°C)			
	3	6	10	16	3	6	10	16
%								
1·9	N	N	N	N	P	ST	T	T
3·3	N	N	N	N	P	P	P	T
4·3	SB	B	DB*	—	SG	VG	VG	—
5·2	DB*	DB*	DB*	—	VG	VG	VG	—
6·1	DB*	DB*	DB*	—	VG	VG	VG	—

N = normal; P = palatable; G = gluey
SB = slightly brown; ST = slightly tallowy; VG = very gluey
B = brown; T = tallowy; * = very insoluble
DB = dark brown; SG = slightly gluey

had been replaced by glucose, causing browning during baking. The browned biscuits themselves showed increased resistance to rancidity.

Crystalline amino-hexose-reductones, produced by the reaction of a secondary amine salt with a reducing sugar, have recently been shown to exert powerful antioxidant effects at low concentrations in hydrogenated vegetable oils and in lard, and their use has been proposed as antioxidants for addition to foods.[84,85]

That conditions which favour browning can powerfully inhibit lipid oxidation is well shown by the work of Banks[10] on dehydrated herring. In this case, not only did pressure cooking at 115° produce a more stable dried product than cooking with open steam, but the pre-cooked herring dried in air at a relatively high temperature was much more stable than similar herring dried at a lower temperature (Fig. 7). The effect of storage temperature was even more striking. At 25° and above, oxidation of the fat was almost completely inhibited, while it proceeded rapidly at 20° and below. A similar although less marked effect has been observed in fish meal, in which oxidation of the oil at 37 or 25°, initially rapid, soon fell away and failed to reach such high levels as at 10°.[86]

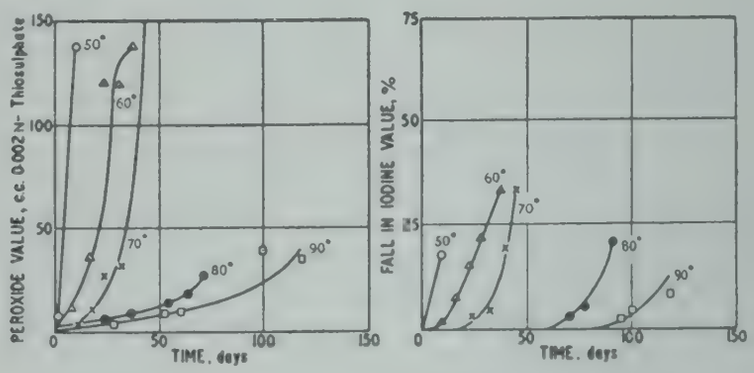

FIG. 7. *Effect of temperature of drying on the stability of dehydrated herrings at* 10° (*ref.* 10)

○ 50° × 70° □ 90°
▲ 60° ● 80°

In the case of spray-dried whole milk, pre-heating the liquid milk to a temperature somewhat higher than required for pasteurization is a widely used means for retarding oxidative changes in the fat of the powder (Fig. 8).[87] In this case the liberation of active —SH groups by the action of heat on the serum proteins is an additional and probably the main factor in increasing stability.

Decreased formation of products of browning reactions may therefore, in a number of cases, explain the greater susceptibility towards oxidative rancidity shown by dehydrated products of very low moisture content. An alternative explanation however has been put forward by Uri,[88,89] who showed that pro-oxidant metals are much less effective in catalyzing the peroxidation of methyl linoleate in polar than in non-polar solvents: he therefore suggests that the protective effect of increasing the moisture content in 'dry' food systems may be due to a weakening of the catalytic activity of traces of pro-oxidant metals present, by the

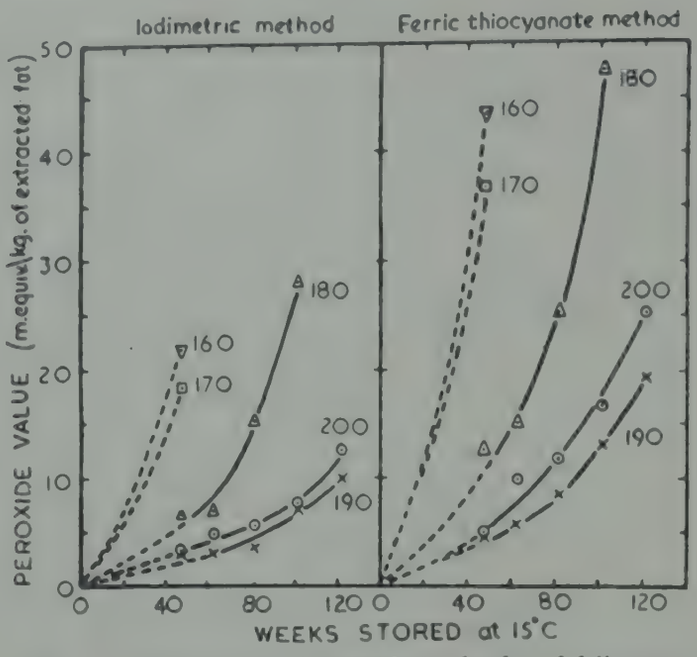

FIG. 8. *Development of peroxide in the fat of full cream milk powders prepared from milk pre-heated at* 160–200°F *and stored at* 15° (*ref.* 87)

introduction of water into the co-ordination shell of the metal. Bawn[90] had proposed a similar explanation for the observation that the rate of the cobalt-catalyzed oxidation of aldehydes and hydrocarbons varied inversely with the amount of water added over the range 0·01–2·0%.

Reactions between oxidizing lipids and protein

Since autoxidizing unsaturated fatty acids in fats or phospholipids give rise to degradation products capable of reacting with free amino and other reactive groups of protein side-chains, it might be expected that browning-type reactions could occur between oxidizing lipids and proteins or amino-acids. Tappel[91] has, in fact, demonstrated the occurrence of such lipid–protein copolymerization reactions in model systems containing linoleic acid or cod liver oil emulsified with protein and an oxidative catalyst (haemoglobin, haemin or cytochrome *c*).

In an attempt to ascertain how far reactions of this type might proceed in stored dehydrated products, a preliminary investigation has been made on fish meal, which contains both high-quality protein and highly unsaturated fat.[86] The oil was found to oxidize rapidly and extensively and both oil and meal darkened rapidly in colour. Some binding of the oxidized oil to protein and some loss of available lysine occurred, amounting to 6–15% of the total extractable lipid (1–2% on the weight of the meal) and 9% of the available lysine respectively in 12 months at 25°. It would appear that, while changes of this type in human foods might well be highly significant from the viewpoint of palatability and colour, they are unlikely to have any very marked effect on the nutritive value of the protein.

Changes in phospholipids and lipoproteins

Phospholipids are of interest in containing both fatty acids (often highly unsaturated) and nitrogen in the same molecule, so that intramolecular browning-type reactions, as well as direct oxidation can occur. Changes in these labile substances are known to be of importance in the storage of dried egg and may well be significant in other dehydrated foods such as dried meat. A review of deteriorative changes involving phospholipids and lipoproteins has recently been published.[92]

Protection by antioxidants

A useful measure of stabilization by the use of antioxidants has been obtained with a number of dehydrated products, and such treatment may be attractive either alone or as a supplement or second line of defence for an oxygen-excluding wrapper or container. The degree of protection obtainable in complex foods, however, is usually well below that produced by direct addition of the same antioxidant to an extracted animal fat.

Gallates,[93,94] preferably the higher gallates,[95] and butylated hydroxytoluene (BHT)[96] have been found of some value in protecting whole milk powder against the development of tallowy ' off ' flavours but, at present, very few countries permit the addition of phenolic antioxidants to milk products. Perhaps of more immediate practical utility is the excellent stabilization of synthetic vitamin-A acetate or palmitate, incorporated into spray-dried skim milk to increase its nutritive value especially for undernourished populations, which has recently been obtained by small additions of antioxidants.[97,98] Antioxidants are now being used on a large scale to stabilize vitamins A and E in dry poultry feeds. They have also been included, together with sulphite, in specifications for dried potato flakes[99] and have been suggested for other dehydrated vegetables for human use.[100]

In air-dried pre-cooked pork early experiments[101] showed that several antioxidants usefully retarded the development of oxidative spoilage in the fat. During 9 months at 20° the treated samples stored in air kept nearly as well as untreated meat stored in an oxygen-excluding pack, and much better than the untreated control in air. At 37° the treated samples in air were perceptibly inferior after one or two months to the meat in the oxygen-excluding pack, owing to the development of ' mealy ' or ' meat-extract-like ' rather than tallowy off flavours, although for at least 4 months they remained superior to the untreated, air-stored controls. Sharp & Rolfe in their contribution to this Symposium[74] report more recent data on the protective effect of antioxidants in vacuum-dried pork.

Antioxidants appear also to show promise as an inexpensive means of controlling the rapid oxidation which occurs in the oil of stored fish meal.[82]

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Discussion

Dr. E. A. H. Roberts (Indian Tea Association): I am interested in the extent to which non-enzymic browning takes place in the course of tea manufacture, particularly during firing. During firing the moisture content of the tea is reduced from about 65% to about 3%, while its temperature rises steadily from about 50 to about 95°. The time required for firing is usually about 40 min. Does Dr. Lea consider that a significant extent of non-enzymic browning is likely to occur under such conditions?

Dr. Lea: In investigations of the rate of reaction of the free amino groups of casein with glucose we found, in systems containing 6–14% moisture, an increase in the rate of reaction of over 1000 times for an increase in temperature from 37 to 90°, the time required for a considerable degree of reaction falling from a few days at the lower to a few minutes at the higher temperature. It would seem that tea is likely to be exposed during the firing process to conditions favourable for protein–sugar interaction.

Mr. E. G. B. Gooding: (1) Would Dr. Lea agree that, when β-carotene is oxidized in dehydrated, scalded carrot stored in air, the first step is oxidation of the lipid in which the β-carotene is in solution, and that the problem in preserving β-carotene is one of preventing lipid oxidation rather than the specific one of protecting the β-carotene itself?

(2) Is there not some confused thinking about the rôle and behaviour of SO_2 in protecting dehydrated vegetables (packed in nitrogen) from browning during high temperature storage? I still hear the statement that ' during storage, SO_2 is lost and can therefore no longer protect the material from browning '. A few years ago Dr. Duckworth and I reported observations which suggested that conditions had to favour the browning reaction before ' loss ' of SO_2 could occur, and subsequent work has confirmed these observations. These conditions might be, for example, high moisture content, scalding with high levels of soluble solids in the scald liquor or high reducing sugar content, as well as elevated temperature. As we saw it, the loss of SO_2 was *necessarily* linked with the progress of the browning reaction; if conditions were such that the browning reaction was not initiated, there was no loss of SO_2. This supports, to my mind, the suggestion made by Dr. Lea that SO_2 blocks the browning reaction by inactivating some colourless intermediate, and that ' loss ' is caused by this mechanism. That loss *allows* browning seems rather to be putting ' the cart before the horse '.

(3) A practical difficulty in applying antioxidants to vegetables before dehydration, is that of getting them into the tissue. Can Dr. Lea suggest how carrot strips, for example, might be treated with a suitable antioxidant?

(4) Dr. Lea said that roller-dried milk is more resistant to oxidation than spray dried. Does he think that roller-dried potato flakes or mashed potato powder would have greater stability in this respect than those dried in the more usual pneumatic dryer?

(5) Would the ferricyanide reducing power be a better way of measuring browning in dehydrated vegetables than the usual aqueous ethanol extraction?

Dr. Lea: (1) Yes. I would say that the oxidation of carotene in an unsaturated fat will be coupled to that of the unsaturated fatty acid residues, so that factors which increase or decrease the oxidative stability of the fat are likely similarly to affect that of the dissolved carotene. Carotene alone, in the absence of fat, also oxidizes quite readily.

(2) No comment is necessary.

(3) The difficulty of securing adequate penetration of antioxidants into a complex structure such as meat, fish or vegetable is, of course, often a major factor limiting their usefulness for such commodities. Antioxidants are usually applied in solution in propylene glycol or edible fat, or in solution or dispersion in an aqueous medium. The case of carrot strip is a difficult one, as found by Lovern in early work in this field and by other investigators since. With dehydrated, finely-divided materials a method which has been found useful in the U.S. is to add an appreciably volatile, fat-soluble, water-insoluble antioxidant such as B.H.A. directly in the solid state; the inhibitor then distributes itself in the lipid phase where it is needed.

(4) I have no knowledge of the relative stabilities of potato dried by these two methods. The moisture content and storage temperature would, of course, have to be low enough for lipid oxidation rather than browning to be limiting in the air-packed material before the stabilizing effect mentioned in connexion with milk could come into play.

(5) The ferricyanide reducing power is a means of following the earlier stages of the interaction of proteins or amino-acids with reducing sugars and of measuring precursors of browning rather than the brown compounds themselves. Since amino-acids are more important than proteins in the browning of dehydrated vegetables, the initial reaction products should be extractable with water or with aqueous ethanol, as used by Wager and by Anet.

Dr. N. R. Jones: My work on codling muscle (reference 52a above) should not be taken as a basis for generalization in the field of fish dehydration; different species vary so much in their metabolism and hence their muscle extractive composition that it is very dangerous to do so.

The reference to Tarr's studies (on Canadian species), stressing the importance of ribose among the reducing sugars in Maillard-type browning, illustrates this danger. Tarr's figures show that there are, in fact, wide variations in the proportion of ribose to glucose. In cod, the most commonly dehydrated species in U.K., we have shown that for reasonably fresh muscle, such as is suitable for dehydration, the sugars available for Maillard reaction are glucose (on the average about 20 mg. per 100 g. of tissue) and ribose with values up to

1–2 mg. per 100 g. Thus, although the ' browning ' potential per unit weight of ribose is about eight times that of glucose, the latter sugar has the greater importance under practical conditions.

Mr. J. T. Hearne: Dr. Lea suggests that lipid oxidation may play a part in development of ' hay-like ' off-flavours; can he give an indication where a reference to this may be found? It is a matter of importance, for development of hay-like flavours may be the limiting storage factor in some cases.

Dr. Lea: The work of F. A. Lee associates ' off ' flavours and discoloration in unblanched frozen vegetables with oxidative changes in the lipids but it is pure speculation on my part to suggest that hay-like flavours in dehydrated foods may perhaps be attributable to a similar cause.

Mr. Joyce: Can Dr. Lea offer any explanation of a phenomenon we have noticed in the vacuum dehydration of apple dice, sugar and small chunks of crystalline root ginger, in which there was a very considerable increase in the strength of the ginger flavour in the product after storage for a month to 6 weeks at room temperature.

A suggestion has been made that volatile components of flavour may be added back to the product. We have had a little experience of this work in connexion with blackcurrants where the true flavour of the fruit is the smell of blackcurrant foliage. We obtained an oleo-resin prepared from blackcurrant buds and this we added to stewed blackcurrants. There was some improvement in the flavour but we found it only possible to obtain the true blackcurrant flavour by dipping a dry, almost flavourless, biscuit into an aqueous suspension of the resin and crunching this in the mouth. It would appear that the volatile compounds responsible for this choice blackcurrant flavour owe their effect to their very rapid volatilization in the mouth at body temperatures. The problem of the volatiles would appear to be very complex and would involve not only chemical factors but certain physical factors such as the dispersion of the volatile compounds themselves in the material.

DETERIORATION OF DEHYDRATED MEAT DURING STORAGE

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E. J. ROLFE

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Introduction

Irrespective of the method of preparation, whether freeze-dried or air-dried, dehydrated meats of good initial quality all suffer deterioration to a greater or less degree during subsequent storage. In the presence of oxygen, the meat becomes unpalatable due mainly to the development of oxidative rancidity in the fat. Although this change can be retarded in certain circumstances by the use of an antioxidant, other changes then become apparent. They are characterized by a yellow or orange discoloration of the meat and by the development of unpalatable, stale, 'mealy' flavours. The chemistry of these changes has not been investigated in detail, but it would appear from certain preliminary observations that the reactions do not take place by the oxidative pathway of the browning reaction.[1]

In the absence of oxygen, it has been proved that the main changes during storage are caused by the Maillard or browning reaction in which the carbonyl groups of reducing sugars react with the amino groups of proteins and amino-acids.[2–9] The meat in this case becomes dark reddish brown in colour and develops first a meat-extract type of flavour and then later in the advanced stage, unpalatable, bitter, burnt flavours. This deterioration in quality is relatively rapid at tropical temperatures and, unless the product is dried to a low moisture content, it may become unpalatable after six months' storage.

The Q_{10} of the browning reaction in meat lies between 3·2 and 4·3 over the range 15° to 50°.[4,8] The rate of the reaction increases with the moisture content of the meat, reaching a maximum at a moisture content equivalent to about 60% R.H.

In addition to the changes in flavour and colour, changes occur also in the power of the protein fractions to reabsorb water and these lead to dryness and brittleness of texture in the rehydrated product.

Up to the present, certain procedures adopted in the production of other dehydrated foodstuffs, such as, for example, the removal of glucose in egg by glucose oxidase or the treatment of vegetables with sulphur dioxide for the inhibition of browning changes, have been found unsatisfactory for meat. The storage life can be extended considerably, however, by drying to very low moisture contents (assisted perhaps by in-can desiccants) and storing at moderate temperatures about 15°. The development of more rapid systems of freeze-drying[10–12] makes it economically feasible to attain the necessary low moisture levels. In Rolfe's method,[10] drying times are of the order of 6–9 hours using commercial-size plant and in Brynko & Smithies' method,[11,12] the drying time is about 4 hours using small-scale equipment.

Spoilage by micro-organisms

Whether or not a micro-organism can multiply in a particular food usually depends on the activity of the water present. The critical factor is probably the osmotic pressure, but its measurement for practical purposes is inconvenient. Osmotic pressure can be related to the equilibrium relative humidity (E.R.H.) of the system and the lowest E.R.H. values permitting development of common spoilage micro-organisms are, according to Mossel & Ingram:[13]

for normal bacteria	0·91
for normal yeasts	0·88
for normal moulds	0·80

In general, it is the water content of a foodstuff and not the E.R.H. that is estimated, and to determine the highest moisture content that can be tolerated without microbial spoilage, it is necessary to refer to the water sorption isotherm.

This function is specific for each foodstuff as it depends on the way in which water is bound by the constituents. Lipids possess no significant water-binding capacity and hence isotherms for meat should relate the E.R.H. with the water content calculated on the non-fatty solids (N.F.S.).

In general, an E.R.H. of 70% gives reasonable protection against microbial spoilage,[13] and the maximum permissible moisture contents for a number of dehydrated meats are given in Table I. The values are derived from the isotherms for cooked and raw beef and other data obtained by Taylor.[14]

Table I

Moisture contents of accelerated freeze-dried (A.F.D.) meats[10] at an E.R.H. of 70% (g. H_2O/100 g. N.F.S.)

	%
Raw beef	18·0
„ lamb	20·0
„ pork	20·0
Minced cooked beef	17·5

In practice, however, the moisture content of dehydrated meat must be well below equilibrium at 50% R.H.[3] in order to reduce the rate of deterioration caused by non-enzymic browning and, therefore, the problem of spoilage from micro-organisms does not arise except under certain conditions of packaging.

Changes due to enzymic activity

Lea's data on the development of free acidity in the fat of dehydrated meat of different moisture contents are given in Fig. 1.[2,15] It would appear from these that lipase is still active in both freeze-dried and air-dried raw beef, especially at the higher moisture contents of 6·7% (N.F.S.) and above. If the meat is cooked before drying, lipase activity in the dehydrated product is insignificant, amounting in meat of 12·2% (N.F.S.) moisture content to a rise in free acidity of the fat after 12 months at 20° from 0·6% to 1·3%, as compared with a rise to 14·9% in dehydrated raw meat of the same moisture content.

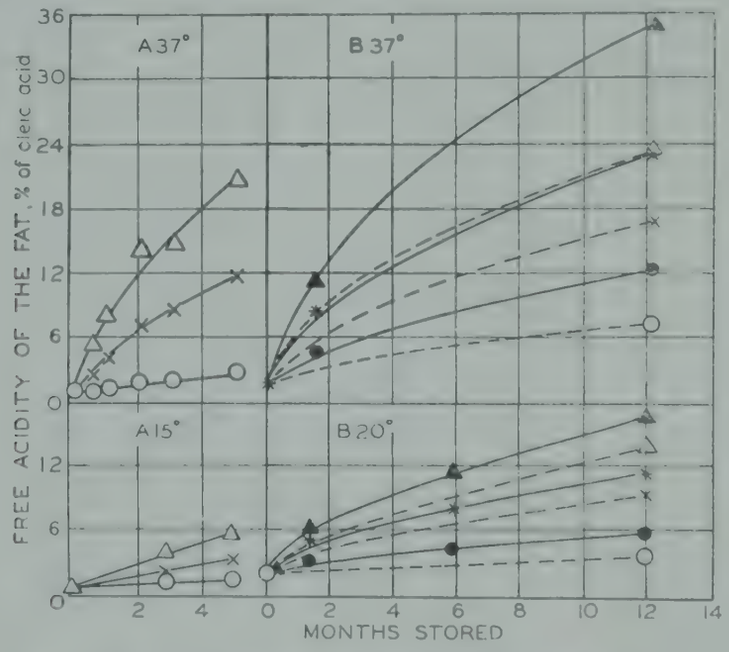

FIG. 1. *Effect of moisture content on the development of free acidity in the fat of dehydrated raw meat*

A. Freeze-dried raw beef containing 6·0, 4·5, and 1·5% of moisture (9·0, 6·7 and 2·2% on N.F.S. basis), stored as a gas-pack containing 0·06 mg. oxygen per g. of meat.
B. Air-dried raw beef containing 7·5, 5·0, and 3·2% of moisture (12·2, 8·1, and 5·2% on N.F.S. basis) stored as a compressed block of density 1·0 in a sealed tin (oxygen contet n0·037 mg. per g. of meat), and as a small block in a large tin (oxygen content 7·8 mg. per g. of meat, indicated by broken line).

Δ 9·0% moisture on N.F.S basis.
× 6·7% „ „ „ „
O 2·2% „ „ „ „
▲, Δ 12.2% „ „ „ „
✱, × 8·1% „ „ „ „
●, O 5.2% „ „ „ „

Kiermeier & Coduro[16,17] quote numerous instances of enzymic activity in dried foodstuffs and have shown that amylase is active in certain cereal products at an E.R.H. of 36% provided that the dry material has a fine capillary structure. It would appear that moisture is condensed in the capillaries at low relative humidities. Freeze-dried raw meat has a capillary structure and it is possible that enzymes such as α-amylase and maltase may be active during storage and produce a supply of reactant sugars for the non-enzymic browning reaction. This may partly explain why dehydrated raw meat is less stable than dehydrated cooked meat; dehydrated minced

cooked meat, for example, containing 12·5% moisture on a N.F.S. basis at an E.R.H. of 60% has a shelf life of approximately one year at 37°, whilst a comparable dehydrated raw meat of 11·0% moisture at an E.R.H. of 54% is scarcely edible after one month at 37°.

At low R.H. of 16% and under, however, it is unlikely that there is much enzymic activity and it would seem, therefore, that deterioration from this source either directly, such as for example by lipase activity, or indirectly by amylase activity, would not be very great. On the data available, the main deterioration, whether in presence or absence of oxygen, would appear to be caused by non-enzymic chemical reactions.

Changes occurring in absence of oxygen

1. *Dehydrated pre-cooked meat*

The changes in freeze-dried, pre-cooked pork stored in nitrogen at different temperatures and at different relative humidities have been studied by Sharp.[3,4] The minced cooked meat was freeze-dried to keep deterioration to a minimum during the actual drying process and after equilibrating to the required R.H., samples were packed in nitrogen for storage. Fig. 2 shows the effects of moisture content and temperature on the rate and degree of discoloration. The corresponding changes in flavour are given in Table II.

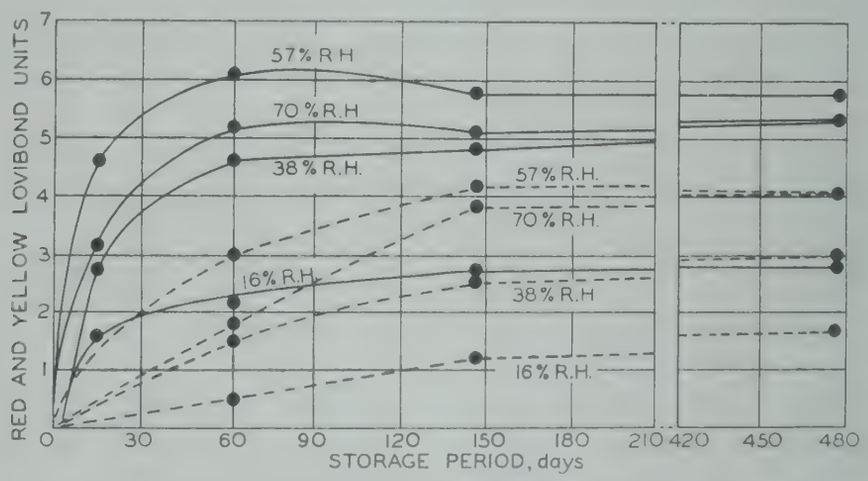

FIG. 2. *Changes in colour of dehydrated pork during storage at different relative humidities (R.H.) in nitrogen at 37° (● - - - - - - ●) and 50° (● ——— ●).*
For equivalent moisture contents see Table II

Table II

Changes in flavour of dehydrated cooked pork of different moisture contents during storage in nitrogen at 37° and 50°

Temperature	37°				50°			
R.H.	16%	38%	57%	70%	18%	38%	57%	70%
Storage (days)								
0	G+	G+	G+	G+	G+	G+	G+	G+
3	—	—	—	—	G+	V. sl. stale, FG	App. roast, FG	V. sl. stale, G
15	—	—	—	—	Sl. stale, FG	App. roast, FG	App. roast, FG	App. roast, FG
62	Sl. stale, FG	Sl. stale, FG	App. stale roast, FG	Sl. stale, FG	Str. bitter, burnt, P	Str. bitter, burnt, P	App. bitter, burnt, RP	App. bitter, burnt, RP
146	,,	,,	App. roast, F	App. roast, F	Str. bitter, burnt, P	Str. burnt, VP	Str. burnt, VP	Str. burnt, VP
477	App. stale, F	Burnt, RP	Burnt, RP	Sour, fruity, P	V. str. bitter, burnt, VP	V. str. bitter, burnt, VP	V. str. bitter, burnt, VP	V. str. bitter, fruity, VP

At 50°C:
16% R.H. = 3·5 g. H_2O/100 g. non-fatty solids (N.F.S.) = 2·0 g. H_2O/100 g. dehydrated meat with 40% fat.
38% R.H. = 6·2 ,, ,, ,, ,, ,, ,, = 3·5 g. ,, ,, ,, ,, ,, ,,
57% R.H. = 10·1 ,, ,, ,, ,, ,, ,, = 5·5 g. ,, ,, ,, ,, ,, ,,
70% R.H. = 14·4 ,, ,, ,, ,, ,, ,, = 7·5 g. ,, ,, ,, ,, ,, ,,

GRADES: Very good (VG); Good (G); Fairly good (FG); Fair (F); Rather poor (RP); Poor (P); Very poor (VP) (inedible); Very slight (V. sl.); Slight (Sl.); Appreciable (App.); Strong (Str.); Very strong (V. str.).

At both 37° and 50°, the rate of development of brown colour increased with moisture content up to equilibration at 57% R.H. and then decreased as the moisture content rose to a value corresponding to equilibration at 70% R.H.

After two months at 50°, the colour reached almost a maximum specific for each R.H. and subsequently increased only slightly over a long period. At 37°, the colour reached almost a maximum after about 5 months. Alongside these changes there was, however, a steady deterioration in the flavour of the samples over the whole period of storage (Table II).

After 5 months, all samples at 50° were unacceptable and all samples at 37° had developed a slightly stale or roast-type flavour and scored only 'fair' to 'fairly-good' in palatability tests. After 16 months, only the sample kept at 16% R.H. was acceptable.

Whilst these changes were occurring, there was continuous production of carbon dioxide and also, in the samples at 57% R.H., total loss after 60 days of the 0·24% of free reducing sugar present initially.

This combination of reactions indicated that the main cause of deterioration was a typical carbonyl–amino browning reaction involving reducing sugars and amino-nitrogen groups in the protein and non-protein fractions of the meat.

Rolfe[18] has observed the changes in flavour and palatability of vacuum contact-plate dried (V.C.D.) minced cooked pork of moisture contents, 2·0 and 14·4 g. H_2O/100 g. N.F.S., corresponding to 3·5% and 65% E.R.H. respectively. His results are given in Fig. 3 and despite the differences in the two systems of taste-panel scoring, they correspond well with Sharp's findings above.

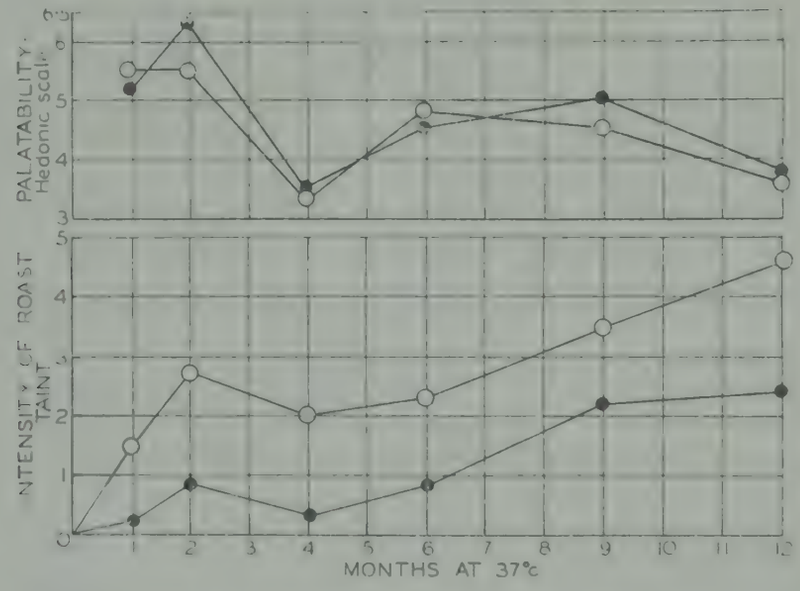

FIG. 3. *Changes in vacuum-contact-dried minced cooked pork during storage in nitrogen at* 37°

Intensity of roast taint: 0 = none; 2 = slight; 4 = appreciable; 6 = very strong
Palatability hedonic scale ranging from 1 = dislike extremely, through 5 = neither like nor dislike, up to 9 = like extremely
● ——— ● 2 g. H_2O/100 g. N.F.S.: 3·5% E.R.H.
○ ——— ○ 14·3 g. H_2O/100 g. N.F.S.: 65% E.R.H.

Fractions in meat responsible for the deterioration.—The part played by the different reactants present in meat was studied by dividing lean pork into an insoluble protein fraction (P) and an aqueous 'solubles' fraction (S) by extraction with boiling water. Aliquot portions of the protein fraction were mixed thoroughly either with aliquot portions of the solubles or with solutions of glucose or potassium lactate containing amounts approximately equivalent to those originally present in the meat, namely 0·1% glucose and 1% lactic acid.

The fermentable sugar was removed from one aliquot of the 'solubles' by fermentation with bakers' yeast and after filtration, the sugar-free extract was mixed with an aliquot of the protein fraction P. The several batches of protein plus the various aqueous solutions were freeze-dried and stored in nitrogen at 50°.

The observations made on the colour and flavour of the batches are given in Table III and Fig. 4 and may be briefly summarized as follows:

(1) No brown discoloration developed in the samples which contained only a trace of reducing sugar.
(2) Lactic acid, which according to the work of Lewis *et al.*[19] was a possible reactant, was found to play no part in the change.
(3) The protein residue reacted with glucose to give a brown product which was, however, relatively tasteless.
(4) The development of brown discoloration together with typical strong burnt flavours occurred only in samples containing both reducing sugar and the aqueous soluble substances of the meat.

Later work showed that (*a*) in addition to the fermentable free sugar present, glucose-6-phosphate might also be present in equivalent amounts as an equally active browning agent, and (*b*) in the presence of 500 p.p.m. of sulphur dioxide, no discoloration developed during 8 months at 50°.

Table III

Initial composition and changes in flavour of dehydrated cooked pork samples during storage at 60% R.H. in nitrogen at 50°

Sample	Equivalents added to 1 equivalent of protein fraction	Composition before storage		Storage period, days			
		Amino N, %	Total fermentable sugar, %	0	28	85	225
PS	1 'Solubles'	0·23	0·25	Fresh, G	App. burnt, FG	Str. burnt, F	Str. burnt, F
P3S	3 'Solubles'	0·53	0·60	Fresh, G	Str. roast, FG	V. str. roast, F	V. str. bitter, F
P4G	4 Glucose	0·04	1·28	Tasteless	Tasteless	V. sl. toasted	V. sl. toasted
PG	1 Glucose	0·04	0·33	,,	,,	V. sl. bready	V. sl. bready
PL	1 K lactate	0·04	0·04	,,	,,	Tasteless	Tasteless
PLG	1 K lactate + 1 Glucose	0·04	0·33	,,	,,	V. sl. bready	V. sl. bready
P	Nil	0·04	0·04	,,	,,	Tasteless	Tasteless
PSF	1 'Solubles' after fermentation with yeast	0·21	0·04	Sl. yeast, FG	Sl. yeast, FG	Sl. yeast, FG	Sl. yeast, FG

GRADES: Good (G); Fairly good (FG); Fair (F); Rather poor (RP); Poor (P); Very poor (VP) (inedible); Very slight (V. sl.); Slight (Sl.); Appreciable (App.); Strong (Str.); Very strong (V. str.).

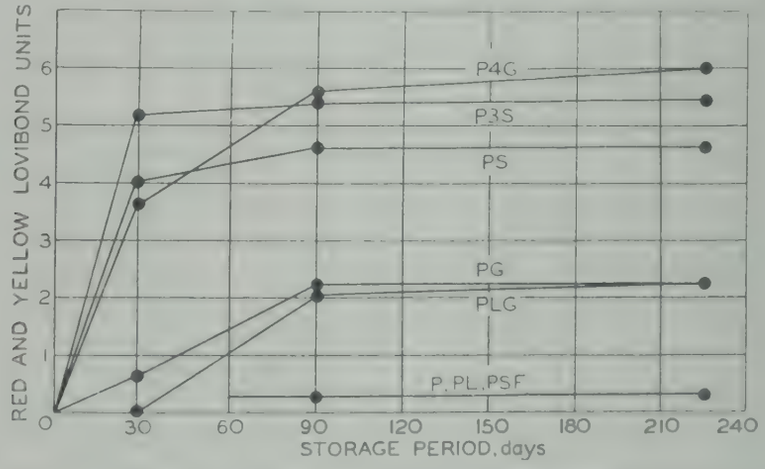

FIG. 4. *Changes in colour of samples of dehydrated cooked pork during storage at 60% R.H. in nitrogen at 50°*
See Table III for composition of samples

Effect of pH on the development of brown discoloration in dehydrated meat extracts.—Since the main flavour changes in meat during storage are caused by reactions in the soluble non-protein fractions, further study was carried out with freeze-dried, protein-free aqueous extracts of pork.[4]

The results of one experiment are given in Fig. 5 and show that the rate of development of brown discoloration increases rapidly with pH in the first period of storage and the increase

in rate per unit of pH is greater the higher the pH. Thus in 12 days, the increases in colour density per unit of pH in arbitrary units are: from pH 3 to 4, 5·1; from pH 4 to 5, 11·2; from pH 5 to 6, 19·2 and from pH 6 to 7, 63·7.

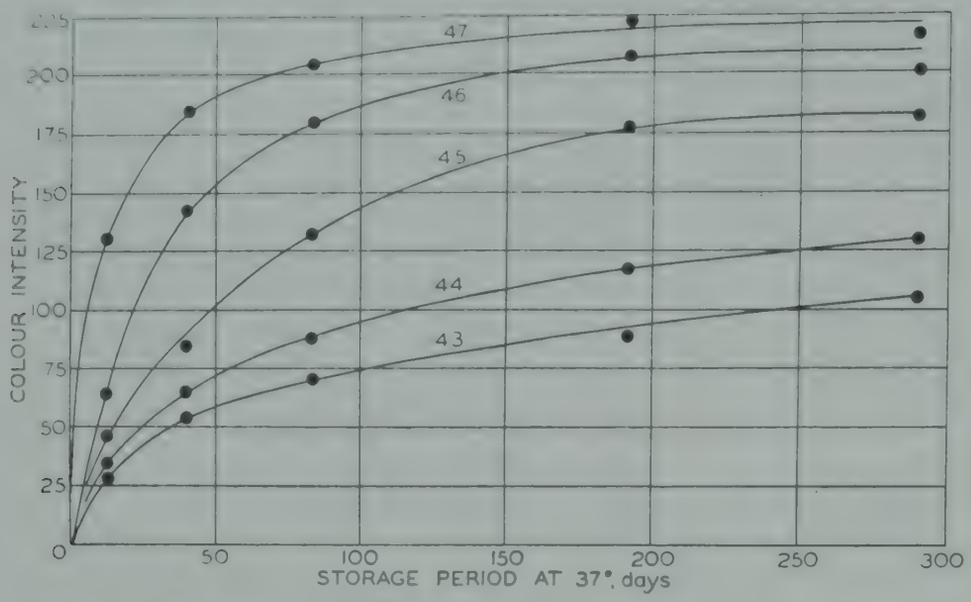

FIG. 5. *Development of brown discoloration in dehydrated extracts of pork of different pH, stored at 60% R.H. in nitrogen at 37°*
(Colour intensity in arbitrary units—E.E.L. colorimeter)

The pH of meat generally lies between pH 5·4 and 6·0, but no appreciable reduction of deterioration is obtained over long periods of storage unless the pH is reduced to about 4. At this pH the meat is too acid to be palatable and therefore, before this procedure could be used to prolong the storage life of either meat or meat extracts, some method would require to be devised to neutralize the excess acid before utilization.

Effect of temperature on the rates of loss of free sugar and development of brown discoloration.—Aliquots of freeze-dried aqueous extracts of pork were equilibrated to 60% R.H. and stored in nitrogen at 15°, 25°, 37° and 50°. Each aliquot contained 5·3 mg. of fermentable sugar of which 4·2 mg. were glucose. Over a period of 16 months, changes in the reducing fractions, colour, fluorescence and pH of the extracts were observed. The more important changes in total fermentable sugar and colour are given in Figs. 6 and 7.

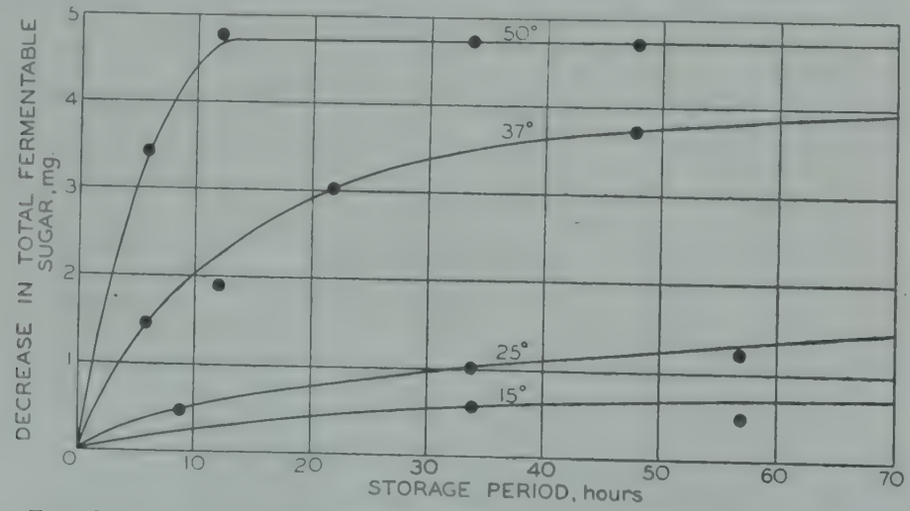

FIG. 6. *Loss of total fermentable sugar (T.F.S.) from dehydrated aqueous extracts of pork during storage at 60% R.H. in nitrogen at different temperatures*

The rates of loss of fermentable sugar and development of brown discoloration in the early period of storage were found to increase steadily with temperature over the range studied. The calculated Q_{10} of the reactions were the same:

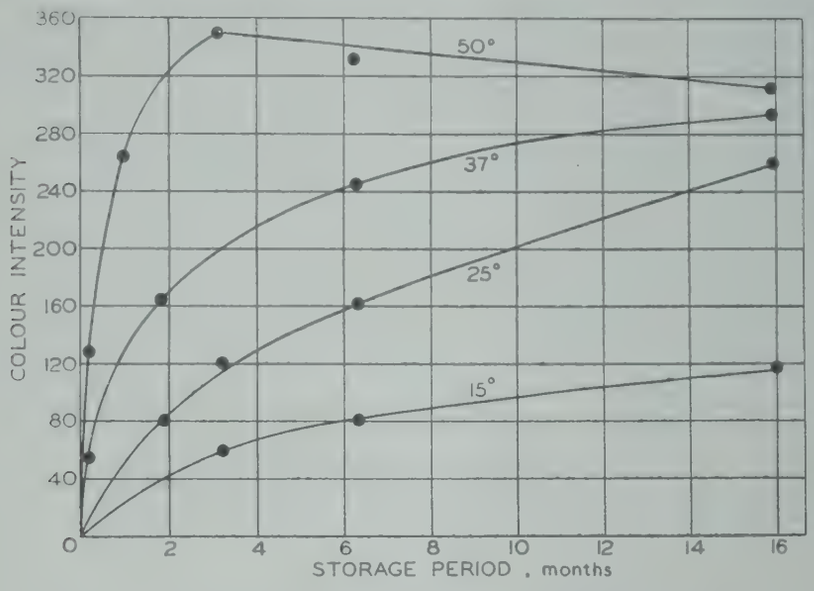

FIG. 7. *Development of brown discoloration in dehydrated aqueous extracts of pork during storage at 60% R.H. in nitrogen at different temperatures*
(Colour intensity in arbitrary units—E.E.L. colorimeter)

	Temperature range		
	15° to 25°	25° to 35°	35° to 45°
Rate of loss of fermentable sugar	4·1	3·4	3·6
Rate of increase in brown discoloration	4·3	3·2	3·5

After 6 months' storage, the samples at 50° had no meat flavour but only a burnt caramel taste; those at 37° and 25° had lost most of the original meat flavour and had a weak, flat taste; and those at 15° still retained a clean, fresh, meaty flavour.

After 16 months, the samples at 50°, 37° and 25° had all developed the usual unpalatable bitter, burnt flavour, but the samples at 15°, although they had become slightly stale, still had an acceptable meat flavour.

2. *Dehydrated raw meat*

The essential difference between vacuum contact-plate dried (V.C.D.)[10] or freeze-dried raw meat and similarly dried cooked meat lies in the state of the protein fractions. In dried raw meat, the proteins are for the most part undenatured and soluble, whereas in dried cooked meat, they are denatured and insoluble. It would be expected, therefore, that the changes taking place during storage of raw meat would consist essentially of the same changes as in cooked meat plus changes associated with the native state of the proteins.

The most obvious difference in the two types of dehydrated meat on storage is in the colour changes. During freeze-drying of raw meat, the oxymyoglobin and oxyhaemoglobin present are deoxygenated to myoglobin and haemoglobin and the meat becomes pink in colour like veal. The changes in colour occurring during storage of accelerated freeze-dried (A.F.D.)[21] beef of different moisture contents packed in oxygen-free nitrogen have been observed by Rolfe[18] and may be summarized as follows:

At 3·3% moisture (N.F.S.) at 20°, the meat was brown after 6 months, became slightly darker in colour over 9 months and turned pinkish brown after 12 months.

At 37°, a similar sample at 3·3% moisture (N.F.S.) and a sample packed with an in-can desiccant which reduced the moisture content to approximately 1% in 3 months, showed in both cases slight brown discoloration after 2 months and increasing browning with time. After 12 months both samples were grey-brown in colour.

At higher moisture contents of 6·3% and 10·8% (N.F.S.) at 37°, samples showed within a month a definite brown discoloration which turned to a yellow-brown in 2 months and a deep red-brown in 3 months. Over a further 6 months, the red-brown colour became darker.

The changes in various palatability factors observed by Hunt & Matheson[20] are given in Figs. 10–12, and in general they are similar to those described previously for dehydrated cooked meat. With the production of brown discoloration there developed the typical flavours resulting from the browning reaction.

Other storage tests have shown that at low moisture levels of 16% E.R.H. and below, the rate and degree of deterioration of freeze-dried raw and cooked meat are very similar; at higher moisture levels, the rate of change is much greater in raw meat than in cooked meat.

Regier & Tappel[7] found that freeze-dried raw meat of unspecified moisture content developed first a grey-brown colour which changed to dark brown over 43 days at 35°. During a further period of 72 days at 54°, the brown colour changed to a yellow-brown. By observations on the absorption spectra of freeze-dried beef, Tappel[1] has shown that even in the absence of oxygen in the atmosphere, metmyoglobin is formed during storage, but the mechanism of this change has not so far been investigated.

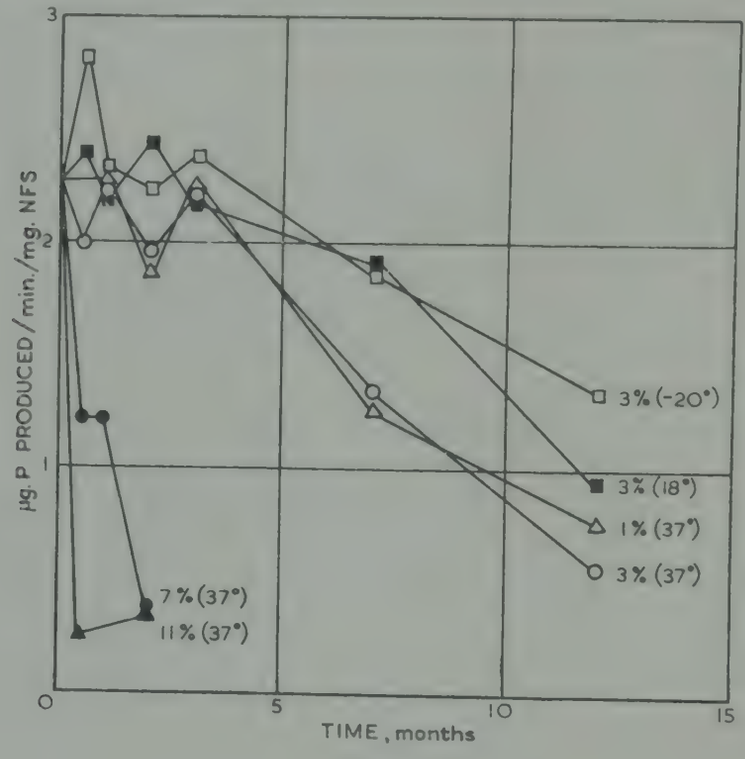

FIG. 8

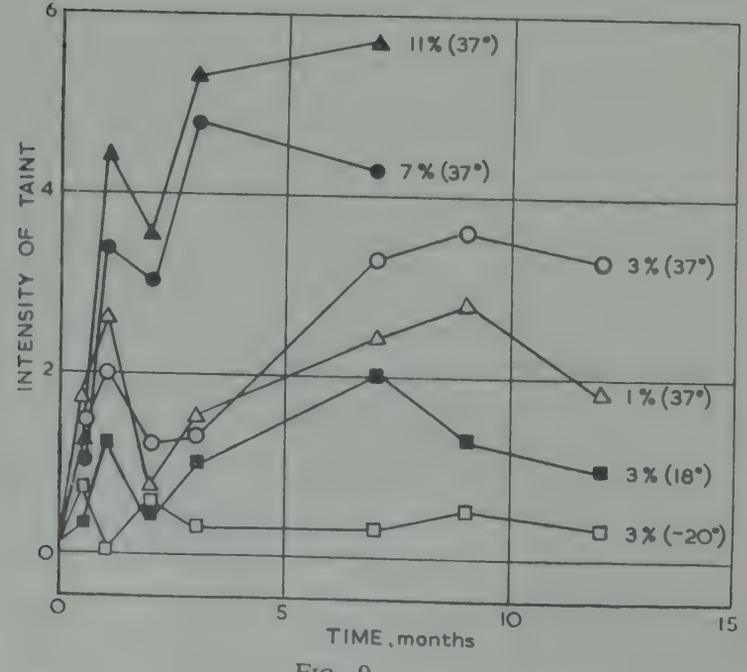

FIG. 9

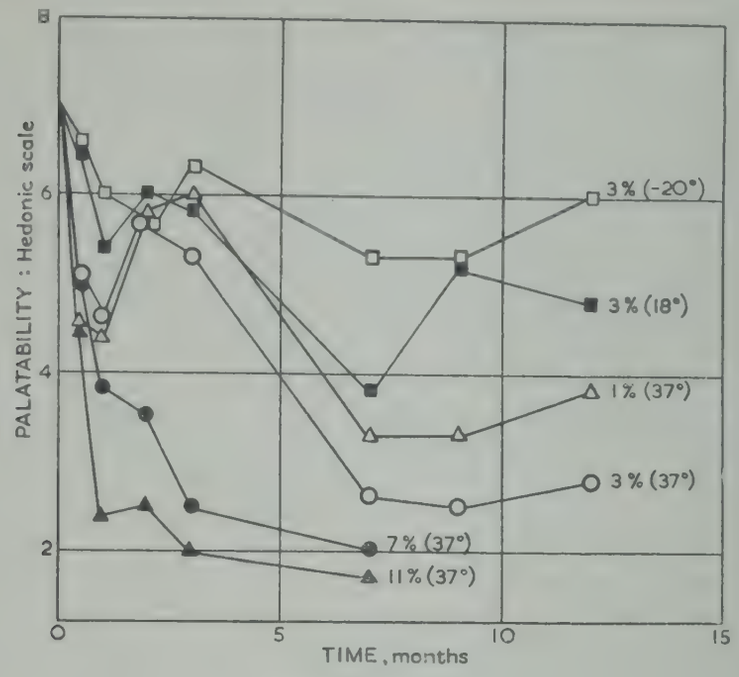

FIG. 10

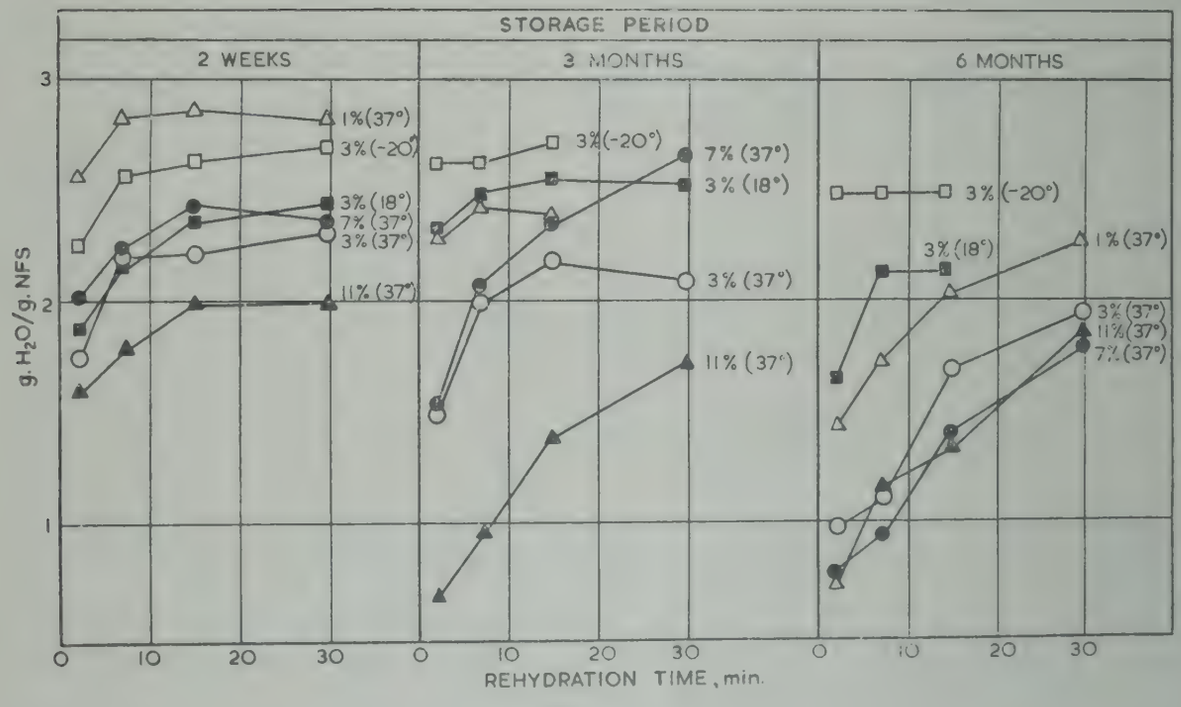

FIG. 11

FIGS. 8–11. *Changes in various attributes of samples of accelerated freeze-dried (A.F.D.) raw beef of different moisture contents during storage in nitrogen at different temperatures*

See text for details of taste panel scales for palatability and intensity of taint and for conditions of rehydration. Values on figures denote % moisture on non-fatty solids basis (N.F.S.) and temperature of storage in brackets ($T°$)

Up to a certain stage of deterioration in storage, the pigments can become reoxygenated to oxymyoglobin by the oxygen in the water during rehydration. Beyond this stage, however, it would seem that irreversible changes may occur in the globin fraction which allow only oxidation to metmyoglobin and not oxygenation to oxymyoglobin to take place during rehydration.[1]

Studies by Regier & Tappel[8] showed that during storage of freeze-dried raw beef in absence of oxygen, the main deterioration was due to carbonyl–amino browning reactions and that the effects of temperature, moisture content and pH were similar to those reported above for freeze-dried cooked meat.

Correlation of deterioration in quality with loss of activity of enzymes.—Since the major protein of meat, actomyosin, possesses enzymic activity to hydrolyse adenosine triphosphate (ATP) to adenosine diphosphate (ADP) and inorganic phosphate, changes in the protein during dehydration and subsequent storage can be followed by measuring its ATP-ase activity. It was considered possible that changes in ATP-ase activity might provide an objective measure of deterioration in dehydrated meat. Hunt & Matheson have recently shown that 40–80% of the original ATP-ase activity of raw meat is retained after dehydration by the accelerated freeze-drying (A.F.D.) process.[20] They have found a correlation between the loss of activity of the enzyme during storage and the general deterioration in palatability of the product.[21]

The small amount of damage to the actomyosin of beef during dehydration by the A.F.D. process is evident from observations on the contractility of the fibres. A sample of dehydrated beef was reconstituted in veronal buffer containing magnesium ions and the reaction of dissected single fibres to the addition of ATP was observed microscopically. The rehydrated fibres contracted, though more slowly and to a less degree, than fibres from fresh beef. It was also found that contractility is not readily destroyed by heating the dried samples. In samples heated for one hour at 22°, 37° and 55°, the fibres were still contractile; after one hour at 70°, they showed reduced contractility and after one hour at 100° had lost all contractility.

Samples from the following storage test retained their contractility after 16 months at −20° and 18°, but were inactive after storage at 37°.

To observe changes during storage, dehydrated raw beef (A.F.D.) was nitrogen-packed in cans and stored under the following conditions:

Sample	Moisture content, g. H_2O/100 g. N.F.S.	E.R.H., %	Temperature, °C
A	3	12·5	37°
B*	3 to 1	12·5 to 5·0	37°
C	3	12·5	−20°
D	7	40·0	37°
E	11	55·0	37°
F	3	12·5	18°

*As A but with an in-can desiccant. Moisture content reduced to less than 1% in 3 months.

Samples were removed from storage at regular intervals and examined (*a*) for ATP-ase activity and (*b*) reconstituted and presented to a taste panel for organoleptic evaluation. In addition to other factors, the taste panel was asked to score palatability by means of an hedonic scale ranging from 1 = dislike extremely, through 5 = neither like nor dislike, up to 9 = like extremely. Taints arising during storage were scored on the following scale: 0 = none, 2 = slight taint, 4 = appreciable taint, 6 = very strong taint.

The decrease in ATP-ase activity in the various samples during storage is shown in Fig. 8. There is a rapid decrease in samples at 7% and 11% moisture content as compared with 3% when stored at 37°. In addition to the adverse effect of high moisture content, the greater damage arising from the higher storage temperature is also apparent.

From Fig. 9 it will be seen that taints developed most rapidly in the samples of higher moisture content stored at 37°. Only slight changes occurred in the samples stored at −20°. Again the adverse effects on quality of high moisture content and high storage temperature are clearly shown.

Fig. 10 illustrates the fall in palatability of the samples during storage. The palatability was found to follow closely the development of taints and loss of flavour, and may be considered to represent an over-all assessment of deterioration in quality. Increases in toughness during storage were small and irregular, whereas small but progressive losses in juiciness occurred, the greatest changes being found in the samples of high moisture content.

The correlation coefficients relating ATP-ase activity and taste panel findings on various attributes were as follows:

Toughness	−0·55
Juiciness	−0·73
Loss of flavour	−0·76
Taints	−0·77
Palatability	+0·84

The correlation between ATP-ase activity and palatability is very high for this type of analysis.

It was thought that changes in the physical state of the actomysin arising from denaturation might lead to a toughening of the tissue and a loss of ATP-ase activity, and that measurements of the latter would reflect the development of toughness during storage. Correlation between these two factors, however, is poor, which would suggest that the damage to actomyosin sufficient to destroy ATP-ase activity is insufficient to produce much toughening.

The rate and degree of rehydration as affected by storage is shown in Fig. 11. Samples of dehydrated beef were immersed in water and removed at definite time intervals. After blotting off superficial water by gentle compression between filter paper, the samples were weighed and the weight of moisture per g. of non-fatty solids derived from the moisture and non-fatty solid contents of the reconstituted samples.

Initially water absorption is rapid and reaches a high level, but with storage the adverse effects of high temperature and high moisture content are soon apparent. Both the rate and degree of water absorption are markedly reduced. Similar changes in the degree of water absorption and the texture of the meat during storage were observed by Regier & Tappel.[7]

Changes occurring in presence of oxygen

The changes occurring during storage of dehydrated meat in presence of oxygen will be considered relatively briefly since, except in special circumstances, the problem of oxidative deterioration will normally be avoided by packing the meat in an air-tight container in an oxygen-free atmosphere.

Dehydrated meats in general, whether raw or pre-cooked, freeze-dried or air-dried, have a large capacity for absorbing oxygen. Lea found that samples of freeze-dried raw beef containing 33% fat and with moisture contents in the range 2·3 to 9·8% (N.F.S.) when stored in air at 37° absorbed oxygen at the rate of 0·18 mg./g./week. A sample of air-dried, pre-cooked beef stored in at atmosphere containing 5·8 mg. of oxygen/g. of meat had absorbed 1·9 mg. of oxygen/g. after 14 months at 20°.

Under quite different conditions, using a Warburg apparatus, Tappel observed in freeze-dried raw beef containing 13–17% fat and 8% moisture (N.F.S.) a very much higher rate of absorption at 38° equal to 0·9 mg. of oxygen/g./week.[1,9]

In freeze-dried raw meat, the immediate effect of oxidation is a change in the colour of the haem pigments which consist of approximately 90% of myoglobin and 10% haemoglobin. After freeze-drying, the meat is bright pink in colour because the myoglobin and haemoglobin are present in the deoxygenated state. With absorption of oxygen, the meat becomes dark brown in colour, due to the formation of the oxidized pigments, metmyoglobin and methaemoglobin. Tappel observed that when freeze-dried beef is held in air at 38°, the colour changes from pink to red-brown in 10 hours, then to brown after 3 days and to a yellow-brown after 20 days.[1]

Alongside oxidation of the haem pigments, oxidation of the fat takes place with the development in time of rancid taints. The amount of oxygen which can be absorbed by the meat before such taints are detectable varies over a very wide range and depends on the degree of unsaturation of the fat and the conditions of drying. Samples of cooked, minced pork, for example, containing highly unsaturated fat may show signs of incipient rancidity after drying in air at 60° to 70° for 4 hours.

After a detailed analysis of the oxidative changes in freeze-dried beef, Tappel came to the conclusion that oxidation of the protein fraction alone could account for at least half of the total oxygen absorbed.[1] In this practically unexplored field, further studies of the oxidation of pure proteins and protein fractions in the dry state should give rise to some very valuable data.

The development of oxidative changes in the lipid fraction can be inhibited by antioxidants but, although the effective incorporation of an antioxidant is relatively simple when dealing with minced meat, it is not a practical proposition with individual pieces of meat such as chops and steaks. In any case, although the oxidation of the fat may be inhibited by antioxidants,

other oxidative changes take place involving the non-fatty components and lead not only to discoloration of the meat but also to the development of unpalatable, stale, ' mealy ' flavours. Tappel found no evidence that oxidative browning reactions involving the reductone–dehydroreductone pathway were responsible for these changes.[1]

Rolfe & Munro[22] have observed the development of a mealy flavour in dehydrated minced cooked meats under two different conditions of storage:

(1) Storage of compressed blocks vacuum-packed in flexible pouches. The mealy taint develops locally where small amounts of oxygen gain access to the meat through the slightly permeable wrap, e.g., M.S.A.T. Cellophane–Pliofilm laminate, or through minute defects in the material or in the seams of pouches made of relatively impermeable laminates.

The meat adjacent to the oxygen supply becomes yellow or yellow-orange in colour and develops the characteristic mealy odour and taste. The remainder of the meat in the pack becomes dark brown in colour and develops the flavour typical of non-oxidative, non-enzymic browning.

(2) Storage in air of loosely packed granules of dehydrated meat containing an added fat antioxidant. In this case, the meat becomes yellow in colour throughout with the development of mealy deterioration. The colour and flavour changes of non-enzymic browning are entirely absent. The mealy odour and flavour are very pronounced in the fat expressed from the stored samples.

The rate of development of mealiness is indicated by the results of the following test on dehydrated minced cooked pork containing 6·6% moisture, 30% fat and 0·1% of Tenox II or Tenox IV based on the weight of fat. The initial peroxide value of the fat was 1·0 mequiv. Samples (2½ oz.) were packed loosely in air in A2½ cans to give an ample supply of oxygen. The behaviour of the meat with both antioxidants was identical. After 4 weeks' storage at 37°, a very slight mealy flavour had developed; after 8 weeks, the mealy flavour was appreciable but the meat was still acceptable; after 16 weeks, however, the taint was strong enough to render the meat unpalatable, and after 24 weeks the meat was definitely inedible. Throughout this period of storage, the peroxide value of the fat had increased to only 4 mequiv. kg. and no rancid taints were detected by the taste panel.

Without the addition of a fat antioxidant, the pork would have been unpalatable after 4 weeks' storage due to rancidity of the fat. The addition of antioxidant, therefore, extends the shelf life of the meat to about 12 weeks.

A few preliminary tests have shown that mealiness does not develop in either the separated fatty or non-fatty fractions alone. It would appear to result from a reaction involving either oxidation products of both these fractions or an oxidation product of one and a non-oxidized component of the complementary fraction. It is clear that the normal non-oxidative browning reaction, which gives rise ultimately to meat extract, roast flavours and brown discoloration, is blocked at some stage when oxygen is present. Greater definition of the reactions involved must await the results of further study aimed at identification of the individual substances which take part in the reaction.

The concentration of reactive reducing substances in meat

The active carbonyl groups which react with amino-nitrogen in the browning reaction are provided in meat by free reducing sugars and certain sugar phosphate esters, principally glucose-6-phosphate, which accumulate in meat post-mortem. In mammalian muscle immediately after death there are present approximately 0·05% of free glucose and 0·05% of glucose-6-phosphate expressed in glucose equivalents. As glycolysis proceeds, the glucose-6-phosphate increases to a maximum of about 0·3% in glucose equivalents and remains at this value during subsequent storage. Only relatively small concentrations of other reducing esters such as fructose diphosphate or fructose-6-phosphate are formed. Simultaneously, if residual glycogen is available, free glucose accumulates together with a smaller proportion of free maltose to give 0·1–0·3% of total fermentable sugar. In the later stages, the maltose is hydrolysed to glucose. The breakdown of glycogen to free glucose takes place quite independently of the Embden–Meyerhof phosphate cycle and continues after the ultimate pH of the muscle has been reached. The three enzymes responsible for the hydrolysis are α-amylase, amylo-1 : 6-glucosidase and maltase. The combined activity of these enzymes, as estimated by the formation of free glucose, varies greatly from species to species. In pork and beef, for example, the rate of accumulation

of free glucose in 24 hours at 18 –20 is 5·7 mg. and 1 mg. g. respectively. This finding explains why the deterioration due to browning changes is usually observed to be greater in dehydrated pork than in beef.

In addition to glucose, Regier & Tappel[7] found evidence for the presence of mannose and fructose in dehydrated beef immediately after drying. The sugars were separated and identified by paper chromatography but no quantitative analyses are recorded.

It is evident from the above findings that under normal conditions of handling meat, the concentration of reducing sugars increases with time post-mortem and, with the object of reducing the potential browning in dehydrated meat during subsequent storage, the aim should be to process meat in which the reducing sugars are present in low concentrations.

This can be achieved in certain animals by lowering the glycogen reserves in the muscle by starvation and or fatigue before slaughter. Callow[23,24] has shown this can be done quite effectively for pigs but it has proved, according to Howard & Lawrie, to be impracticable for beef animals in which the stores of glycogen are maintained at a relatively high level.[25]

In the second place, the meat could be prepared and dehydrated soon after the death of the animal and before any appreciable accumulation of reducing sugars had taken place. This procedure, although quite practicable in small-scale production, is not very suitable for large-scale production and in any case may lead to the production of a rather tough product.

If the meat is to be held for only 1 to 3 days before being processed, the rate of production of free sugars in the meat can be reduced by lowering the temperature as quickly as possible post-mortem and holding the meat in the chilled state at 0° to 3°.

If the meat is to be held for longer periods, the accumulation of free sugars can be almost completely inhibited over a long period by freezing the meat immediately post-mortem and holding it at temperatures of −10° or below. This last procedure would appear to be particularly appropriate to the latest developments in freeze-drying as described by Rolfe[10] and Brynko & Smithies.[11,12]

Summary and conclusions

(1) In presence of oxygen, the main cause of deterioration in quality of dehydrated meat during storage is oxidative rancidity of the fat. If this type of oxidation is inhibited by means of an antioxidant, other oxidative changes take place and lead, in the presence of both the fatty and non-fatty fractions, to the development of a yellow-brown discoloration and unpalatable, stale, ' mealy ' flavours.

(2) In absence of oxygen, there is no significant deterioration in the fat, but carbonyl–amino browning reactions take place in the non-fatty fractions with the development of red-brown discoloration accompanied, in the early stages, by meat extract, roast-type flavours which change to unpalatable, bitter, burnt flavours in the later stages of storage. These changes appear to be inhibited when oxygen is present.

(3) Corresponding roughly in degree with the changes in colour and flavour, changes in the physical properties of the protein fractions occur simultaneously. These changes cause a decrease in the power of the proteins to reabsorb and hold water, with the result that the rehydrated meat has a much drier and more brittle texture.

(4) The browning reactants present in meat are free reducing sugars, mainly glucose and the ester glucose-6-phosphate, which react with the amino- and imino-groups of the proteins and the soluble amino-acids. The changes in flavour are caused mainly by interaction of glucose with the aqueous soluble amino-acids present.

(5) The rate of browning increases with pH and also with moisture content up to a maximum at an R.H. of 60%. No appreciable inhibition of browning deterioration is effected over long periods of storage at temperatures of 37° and above, unless the moisture content of the meat is reduced to the equivalent of 16% R.H. or lower. This means a moisture content of 3·5% on a non-fatty solids basis or 2% in meat with a fat content of 40%.

(6) Dehydrated raw meats are less stable during storage than dehydrated cooked meats, particularly at higher moisture contents equivalent to 60–70% R.H. In addition to changes associated with the denaturation of the proteins, it is possible that this difference may be partly due to the survival of enzymic activity in the raw meat resulting in the production of substances which promote non-enzymic browning.

(7) During dehydration by the accelerated freeze-drying process, beef muscle myosin suffers only slight deterioration. The muscle fibres on rehydration are still contractile and retain 40–80% of their original ATP-ase activity. During storage of such dehydrated beef, particularly at elevated temperatures (37°), the deterioration in several palatability attributes is closely paralleled by loss of ATP-ase activity. It is probable, therefore, that the loss of ATP-ase activity might form the basis of an objective test of quality in dehydrated raw meat.

(8) The Q_{10} of the rates of loss of free fermentable sugar and development of brown discoloration over the range 15° to 50° are the same and lie between 3·2 and 4·3.

(9) The reactants, free glucose and glucose-6-phosphate, are both present in meat immediately after the death of the animal to the extent of only 0·05% in glucose equivalents. Within 24 hours at 15°, however, the glucose-6-phosphate accumulates to reach a maximum value of about 0·3% in glucose equivalents. Free glucose may accumulate continuously as long as glycogen is present, and in pork may reach values of 0·6% after a week at 0°.

(10) In order to have the browning reactants present at low concentrations, the meat should be dehydrated either immediately after the death of the animal or it should be held either in the chilled state at 1°–3° or preferably frozen and stored at temperatures of −10° or below.

(11) Although the browning changes can be inhibited in laboratory tests by treatment with sulphur dioxide or by removal of reactive sugars by fermentation, neither of these procedures is practical in large-scale production. The only practical procedure at present for the preservation of quality in dehydrated meat over long periods of storage is to dry the meat to a low moisture content equivalent to 16% R.H. or lower, to pack it in an air-tight moisture-proof container in vacuum or in an oxygen-free atmosphere and to store it at a low temperature, certainly not higher than 15°, for the greater part of its storage life. The recent development of newer procedures in freeze-drying makes the attainment of such low moisture contents possible within a drying period of 4–6 hours.

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THE INFLUENCE OF THE CONDITIONS OF DEHYDRATION ON THE QUALITY OF VACUUM-DRIED MEAT

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Introduction

During the Second World War considerable effort was expended on the development of methods for the production of stable palatable dehydrated meats, and procedures were established for the preparation of dehydrated minced cooked beef and pork.[1–3] Large quantities of dehydrated minced cooked meats were prepared by hot-air drying in various parts of the world, but the usefulness of such products is limited as they can be included only in made-up dishes. Attempts to dry larger pieces of cooked meat, e.g., ½-in. cubes, by this process were not encouraging. Lean tissue in contact with adipose tissue required a very long period to dry and it was found necessary to select carefully lean meat in order to avoid a serious lack of uniformity in water content throughout the final product. Even so, drying was protracted, thus reducing the quality of the product: at a tray loading of 2 lb./sq. ft., drying to an average of 8% moisture content required 12–22 hours for the cooked cubes, but only 4 hours for cooked minces. The drying of raw meats even in the mince form by means of hot air was also impractical because of the long drying period required and, in addition, the product was of inferior quality as compared with the dehydrated minced cooked meats.[3]

The vacuum drying of meats was also studied[4] but it was not until the post-war years that developments in vacuum drying permitted dehydration of meat in steak and chunk form, to give products resembling closely the original fresh meats.

Vacuum drying may be subdivided into two general procedures:

(1) Evaporation of water from the liquid phase.

(2) Sublimation of water from the solid (frozen) phase.

These two procedures produce materials with markedly different properties.

Vacuum-drying of meat. Evaporation of water from the liquid phase

(*a*) *General considerations*

Water can evaporate only from the surface of a piece of moist tissue subjected to a vacuum and where freezing is not allowed to occur. During migration to the surface, the water will transport dissolved salts and soluble proteins, so that evaporation will lead initially to a concentration of the soluble constituents at the surface. Further drying produces a dry glossy skin or pellicle around the tissue as moisture is lost more quickly than it can be replaced by migration from within. The pellicle consists of the soluble proteins transported to the surface together with the structural proteins possibly solubilized by the increased salt concentration. The surface of the tissue becomes dry as moisture is lost more quickly than it can be replaced by migration from within.

The tissue is soft and plastic and is unable to resist volume changes while its bulk is being reduced by moisture losses. The meat therefore shrinks, acquires a wizened shrunken appearance and becomes much darker in colour. Dehydrated cooked meat is often a blackish brown colour.

The temperatures in the material are lower during vacuum-drying as compared with drying by hot air,[5] so that damage to heat-labile compounds and deterioration due to chemical reactions is reduced, e.g., in a comparative test on the drying of a cooked pork mince, hot-air drying gave a product with no residual reducing sugars (they had been consumed in the initial reactions of non-enzymic browning), whilst an appreciable proportion remained in the vacuum-dried mince. Damage to the more labile compounds is shown by changes in the raw meat proteins so that the dry tissue is not only unable to absorb as much water during reconstitution as was originally present, but it is also less retentive. Cooking in the absence of water, e.g. frying, drives off much of the imbibed water and the meat becomes very tough and leathery in texture. Cooking in water, e.g., for stews and casseroles, prevents evaporative losses of moisture in the reconstituted meat but the meat is still more tough and less juicy than the starting material. The dehydrated meat also has a weaker flavour; presumably loss of volatile constituents is at least partly responsible. It has been shown that volatile sulphur compounds are important components of chicken flavour.[6]

Reconstitution of vacuum-dried meats is hindered by the external glossy skin and the denseness of the dry tissue.

(*b*) *Histological changes*

Wang *et al.*[7] have studied this aspect. Longitudinal and transverse strips of beef muscle biceps femoris, both raw and pre-cooked, were examined and no appreciable difference was found in meat dehydrated at 65° in a vacuum of more than 25 in. Hg and that dried at 70° in a mechanical convection air oven. Drying times were 20–24 hours. Loss of water from the tissue was slow and accompanied by diminishing endomysial spaces, progressive reduction in muscle fibre diameter, merging of muscle fibres, disappearance of longitudinal striations, decreasing distinctness of cross-striations in muscle fibres and movement of potassium to the periphery of muscle fibres. Apparently potassium moved with the water to the periphery of the fibres, but was not able to move through the membrane at the muscle fibre–connective tissue boundary.

Pre-cooked meat exhibited a more rapid loss of moisture during the early stages of dehydration and dehydrated to a lower moisture level than did raw meat. With both raw and pre-cooked samples, transverse slices dried more rapidly than longitudinal slices during the early stages of dehydration. This is readily explained if it can be assumed that water movement parallel to fibre direction may be more rapid than diffusion perpendicular to the muscle fibres. Thus during the early stages of dehydration of transverse slices, the rate of drying would be limited by the speed of water movement to the surface through the endomysial spaces, but later the slow diffusion through the fibre membrane would become limiting.

The relationship between shrinkage of muscle fibre diameter and moisture loss during the dehydration under the above conditions was examined and a correlation coefficient of 0·65 was calculated. It, therefore, appears that moisture loss accounts for about half of the total factors influencing fibre shrinkage.

The dehydrated meats held in water at 70° for 15 min. did not absorb much water, and it occurred to Wang *et al.*[8] that peripheral movement of potassium in muscle fibres in dehydrated meat might lead to irreversible protein denaturation at cell boundaries restricting re-entrance of water.

If so, removal of the potassium ions by electrolysis prior to dehydration might prevent protein precipitation and a more rehydratable end-product obtained. During electrolysis, the pH of the beef fell from 5·5 to 2·8 and the muscle fibres became swollen due to water absorption. The normal endomysial spaces disappeared and were replaced with a new system of irregular spaces, some of which were retained on dehydration. When dehydrated together with untreated controls at 70°, the products were similar in most respects, the muscle fibres being tightly packed with extensive merging. The dehydrated electrolyzed samples rehydrated readily to about 70% moisture content (in fact they inbibed water to a point where they would fall apart in a few minutes) whilst the controls absorbed water only to 30%. The diameter of the muscle fibres of the reconstituted electrolyzed samples did not, however, increase appreciably and cross-striation did not become much more distinct, but the system of irregular spaces induced by electrolysis were retained. The exceptions were three samples of electrolyzed rectus femoris muscle which apparently reconstituted in the 'true' sense (as defined by the authors) as they recovered their muscle fibre diameter, had the spatial organization normally present in fresh raw meat with little merging of muscle fibres and exhibited distinct cross-striations in most of the muscle fibres. No adequate explanation for this behaviour could be found.

As a criterion for true reconstitution, the authors used the reappearance of distinct cross-striations of the muscle fibres, basing this on recent views[9] regarding their nature, namely that the striations represent the physical manifestation of the molecular configuration of the actomyosin complex of the muscle.

Carcass grade and extent of ageing had no significant effects on the moisture relationships or muscle fibre diameter of raw beef dehydrated at 70°.

(*c*) *Vacuum-drying processes*

(1) *Vacuum contact-plate dehydration.*—Possibly the most difficult problem in the vacuum-drying of meats is to provide an adequate supply of heat to replace quickly evaporative heat losses. Simple plate or shelf vacuum-dryers supply heat mainly to the underside of the drying tissue, and as contact between the plate and tissue may be poor due to shrinkage and distortion

of the drying meat, heat transfer becomes poor and drying times are prolonged. Increased heat transfer could be obtained by raising the plate temperature, but at the cost of excessive heat damage of adjacent tissue.

A solution to this difficulty has been found in the vacuum contact-plate (VCD) process. The plant[10] consists of a vacuum-tight steel cabinet containing a vertical bank of horizontal hollow steel plates. Hot water is circulated through the plates to provide the heat for evaporation and the plates can be moved together to sandwich the material and provide good thermal contact. In this way not only is heat applied to both top and bottom surfaces to accelerate drying of the tissue, but by lightly squeezing the material, shrinkage away from the plates during drying is prevented and good thermal contact is maintained with the meat throughout the drying process. A charge of 740 lb. of raw beef cut into 1-in. cubes can be dried to 3% moisture content in $7\frac{3}{4}$ hours.[11]

At the beginning of the drying process there is a rapid loss of water from the meat permitting the heating plates to be operated at 100° and the absolute pressure in the chamber is of the order of 10 mm. Hg. The rate of evaporation from the tissue gradually decreases due to the progressively slower diffusion of moisture to the surface. To avoid over-heating the tissue, the heating plates are allowed to cool to 60° and at the same time the vacuum improves to 2·5–3 mm. Hg absolute pressure. During the early stages of drying the meat temperatures are between 20° and 30° and only when drying is almost complete and evaporative losses are small does the meat finally reach 60° (as can be seen from Fig. 1).

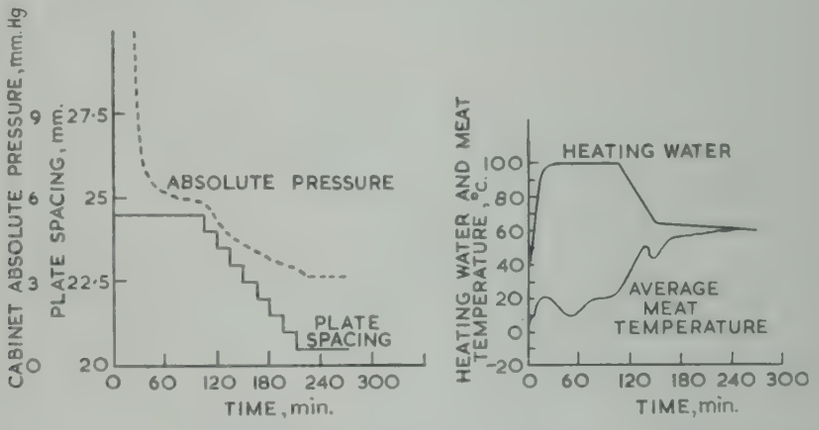

FIG. 1. *Graph illustrating the procedure developed for the drying of frozen raw beef slices by the VCD process*

Initial thickness of slices 15–18 mm., thickness of tray and lid 5 mm., tray loading approx. 1 lb. 10 oz./ft.,^{2} final moisture content 4%, initial weight 363 lb., final weight 137 lb., 7 trays (8 ft. × 4 ft.)

The dehydrated raw meat is dark red in colour and with a rather glossy surface free from pores. The tissue is dense and when broken open is seen to be made up of a system of merged muscle fibres. The density is around 0·6 g./c.c. If immersed in cold water it will slowly reconstitute (2-4 hours), the reconstitution water being stained red by meat pigments, but provided sufficient water has been absorbed to render the dehydrated meat plastic it may then be used for cooking in a stew, pie, etc. Attempts to cook dehydrated meat that is still hard in parts can result in the development of a marked processed flavour probably due to induced non-enzymic browning in the dry tissue at the temperature of cooking before reconstitution intervenes.

Because of structural changes and denaturation of the proteins, reconstitution is incomplete and the water is loosely held, much of it possibly by capillarity. The eating qualities, are, therefore, inferior to those of fresh meat, particularly as regards texture.

Pre-freezing the meat effects a considerable improvement in quality of the dehydrated raw meat. It facilitates drying so that the tissue is subjected to a less severe heat treatment (a drying time of $4\frac{1}{2}$ hours has been achieved) and also provides a somewhat porous structure in the dry product, its density being 0·3-0·4 g. c.c. The glossy skin is less pronounced. The latter two factors are no doubt responsible for the improved speed of reconstitution. Most water is absorbed during the first two hours reaching 2·3-2·8 g. water g. non-fatty solids (NFS) (see Fig. 2)

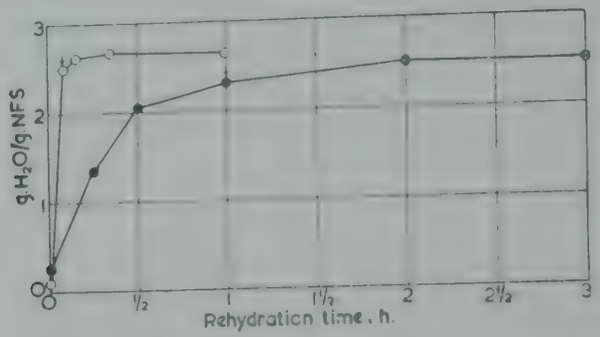

FIG. 2. *Reconstitution curves*

○ = Accelerated freeze-dried raw sliced beef
● = Vacuum contact-dried raw sliced beef pre-frozen before drying
At the time indicated by the arrow the samples were ready for cooking

and generally thereafter increasing by only 0·1 with immersion up to 24 hours. The most striking result was obtained in the dehydration of pre-frozen beef psoas muscles. The product was a porous tissue which within 1 hour had absorbed water equivalent to 3·4 g./g. NFS and was even tender and juicy when fried. Dehydrated pre-frozen meat is a bright carmine colour, and is sufficiently different in appearance from the brownish red colour of dehydrated chilled meat as to make the two products readily distinguishable.

Ageing or conditioning of beef before drying gave only a very slight improvement in texture of the dehydrated product.

(2) *Vacuum-drying in molten fat or oil.*—In this process very good heat transfer to the tissue is achieved by immersion in heated fat. During the drying process the tissue becomes impregnated with fat which can be subsequently removed. Platt & Heard[12] patented a process of this kind for the drying of leafy and root vegetables, meat and fish. The foodstuff, cut into suitably sized pieces, is immersed in a non-aqueous liquid (edible fat or hydrocarbon) and heated to destroy enzymic activity. Thereafter moisture is removed from the foodstuff at around 80°. The oil may be removed from the dry product by centrifuging or solvent extraction. The dehydrated meat is dark and generally brown in colour, and may be reconstituted by soaking in hot or cold water.

Drying times under laboratory conditions at 26-in. vacuum are shown in Table I.

Table I

Drying by Platt & Heard process[12]

	Time, min.	Residual water content, %
Spring greens	45	2
	35	4
Cabbage	90	2
Peas (green)	75	7
Potato slice raw	53	15
„ precooked	40	7
Raw beef mince	130	14

It is evident that water is removed with comparative difficulty from raw meat.

Zimmermann[13] employed a similar process during the Second World War to prepare a wide range of dehydrated foods, e.g., bacon with beans, roast beef with cream sauce, curried beef and various meats. He found that dried ready-cooked foods of animal and vegetable origin could be dehydrated in the presence of edible fats by controlled heating above the boiling point of water in vacuum until a stable dry product is obtained. He claimed that the cavities and intercellular spaces arising during the dehydration became filled with the fat or oil and when the dry product was placed in warm water at a temperature above the melting point of the fat, the fat was expelled from the tissue and replaced by water and vegetable and animal tissues became identically restored to their original state. The consumer was instructed to cook the dehydrated foods in 1–3 times their volume of water for 15 min.

Zimmermann found that raw meats dehydrated in this manner did not always swell satisfactorily when cooked in water.[14] He attributed this to failure of the fat to fill completely

the intercellular spaces left by evaporation of water during dehydration, and suggested the remedy of temporarily breaking the vacuum during the drying cycle and allowing atmospheric pressure to force the molten fat into the intercellular pockets of the material.

He claimed that the flavour and texture could be improved by partial breakdown of the meat proteins by mineral acids, alkalis, protein-splitting enzymes, e.g., pepsin or trypsin, or by hydroxy-carboxylic acids, e.g., lactic acid.[15,16]

The important finding made by Zimmermann, and in which his process is an advance compared with that of Platt & Heard, is the improvement in the quality of the product obtained by pre-freezing.[17] He instructed that the raw meat be cooled to a temperature below zero, e.g., −6°, and then placed in the fatty substances heated above the coagulation temperature of the meat proteins, preferably at 80°–84°.

In this procedure Zimmermann's object was to coagulate the surface proteins and thus prevent leaching of flavour and nutritious matter during reconstitution of the final dry product. It is doubtful if such a procedure would be successful in achieving this object, but, by employing pre-frozen meat in vacuum-drying, a more palatable product is obtained and drying is facilitated.

In New Zealand the dehydration of raw meat in vacuum using molten fat as heat-transfer medium has been studied, and the process developed to a full-scale production unit.[18]

Boneless frozen meat is cut into pieces 3 × 3 × ½ in. with the grain of the meat parallel to the ½ in. dimension and dropped into molten fat at 160°F. The water is distilled off under vacuum (1 in. Hg or less) at relatively low temperatures below 120°F. During the drying process (usually less than 4 hours) the temperature of the meat gradually rises to 160°F and the moisture content of the raw meat falls to less than 5%. The surplus fat is removed from the dry product by spinning in a centrifuge for 3 min.

Unless the meat is pre-frozen, it shrinks considerably, hardens during the drying process and the rate of drying is much slower. Without pre-freezing it proved difficult to reduce the moisture content below 10%.

The dry product is hard, somewhat porous and reddish brown in colour. In reconstitution and cooking qualities it closely resembles frozen meat dried by the VCD process.

Vacuum-drying of meat. Evaporation of water from the solid phase

(*a*) *General*

These procedures involve the removal of water from frozen tissues by sublimation of ice crystals. There can be no migration of water and hence no transport of soluble constituents. As the surface water is lost the drying front recedes within the tissue, and case hardening is prevented. The frozen tissue is rigid and with removal of ice crystals a porous, low-density material with the original dimensions remains. The porous structure facilitates reconstitution and the low temperatures employed during the drying process keep to a minimum the damage to the structural proteins and the deteriorative chemical changes. Consequently the products conform more closely to the natural texture and structure of the original meat.

The early procedures were expensive and for this reason were applied mainly to biological substances. Flosdorf, who was active in this field, published a review of the early developments in 1949.[19] Meat is an expensive food, and it is possible that the added cost of dehydration by one of the more recent developments in freeze drying will be a sufficiently small proportion of the raw material cost to make the process economic.

(*b*) *Procedures*

(1) *Conventional freeze-drying of meat.*—A considerable amount of work on this subject has been done in America and a useful review of present knowledge had been published by Harper & Tappel.[20]

Freeze-drying has been successfully applied with a minimum amount of physical and chemical changes to the drying of thermolabile biological materials, e.g., bacteria, viruses, tissue skin, etc.[19,21]

The procedure can, therefore, be expected to be ideally suited for the drying of such foods as meat. The meat may be frozen preparatory to freeze-drying either by pre-freezing in external freezing equipment, or by evaporative freezing in the drying cabinet. Harper & Tappel recommend the former as the latter process permits sufficient surface drying to take place in the unfrozen state for some case-hardening to occur.

With the pressure at approximately 1 mm. Hg, freeze-drying proceeds by sublimation of the ice from the surface and the ice-front gradually recedes within the product. According to the design of the equipment used, the heat must reach the evaporative surface through either a layer of frozen material or dried material. In the former instance the temperature of the plate supplying the heat must be kept below freezing point. In the second case the heat must flow through a dry porous layer of low thermal conductivity (thermal conductivity of frozen meat is about 1·3 B.Th.U. h. ft. °F and of freeze-dried meat about 0·02 B.Th.U. h. ft. °F) and the surface temperature of the heating plate is limited by the thermal sensitivity of the dried meat. Excessive temperatures will lead to browning of the meat surfaces and the development of processed flavours in the product. Tappel *et al.* examined the freeze-drying of 1-in. slices of beef, biceps femoris, using infra-red radiant heating and on hollow shelves heated by hot water.[22] Vacuum-drying at temperatures of 0–15° and 30–45° and absolute pressures of less than 23 mm. Hg gave extensive case-hardening of the beef pieces. Drying times were very long and organoleptic properties of the beef were poor (see Table II). (Comparing this result with that from the VCD process, the advantage of the latter system of heating plates can readily be appreciated.) Tappel states that ' this study shows that the theoretical engineering advantage of some rapid heat transfer at temperatures above freezing cannot be realized because protein denaturation at the surface limits the outward diffusion of water.'

Table II

Vacuum dehydration of 1-in.-thick biceps femoris muscle

Plate temp.	Time in vacuum oven, h.	Final moisture content, %	Rehydration in 1 h.	Organoleptic observations		
				Colour	Texture	Flavour
0–15°	60	20	30%	Dark brown	Dry	Roasted
30–45°	65	7·5	30%	Dark brown	Dry and stringy	Browned

In spite of case-hardening, very much more rapid drying is obtained using VCD equipment and it would seem that heat transfer in Tappel's vacuum oven was not so rapid as he suggests, possibly due to the shrivelling and wrinkling of the meat that occurs during the drying cycle which would prevent good contact with the heated plate being maintained. Plate closure in the VCD plant maintains good plate contact by preventing the meat from shrinking away from the heating plates.

Tappel found that 1-in. slices of meat could be dehydrated more quickly by freeze-drying to yield a superior product. Heating with infra-red radiation was difficult to control and localized over-heating was a problem. Both methods of heating gave the same drying time of 24 hours to 10% moisture.

The properties of freeze-dried beef biceps femoris muscle are shown in Table III.

Table III

Properties of freeze-dried beef biceps femoris[23]

		Organoleptic observations after rehydration and cooking	
Composition	80–85% protein, 13–17% lipid	Flavour	Same as frozen control
Moisture content	3% for 1-in. thick pieces in freeze drier for 24 hours	Texture	Generally drier than control
Structure	Like balsa wood—no volume change during freeze drying	Appearance	Same as frozen control
Density	0·33 g./c.c.		
Porosity	80%		
Thermal conductivity	0·02 B.Th.U./h./ft./°F		
Colour	Pink		
Rehydration 1 h.	80–90%		

The rate of reconstitution is primarily dependent upon the rate of flow of water through the capillary-like openings into the central portions of the blocks of meat. The meat proteins themselves reconstitute very rapidly.

Reconstitution of whole pieces becomes rapid (5 min.) when the air is evacuated from the dried beef beforehand, e.g., by opening a vacuum pack under water. The level of reconstitution

is high, 80–90%, but after cooking, the texture is usually more dry than that of controls, indicating less tenacious bonding of the water.

Wang *et al.* have studied the effect of various freezing methods on the structure and reconstitution of freeze-dried beef.[24] The conditions used were:

(i) Immersed 3 min. in *iso*pentane cooled to −150° by liquid nitrogen (rate of freezing is increased five-fold by substituting *iso*pentane at −150° for liquid nitrogen at −195° due to the better heat-transfer across the boundary[25]).

(ii) Using dry ice at −90° for ½ hour.

(iii) Cold room at −17° for 6 hours.

Pre-frozen at −150°. After freeze-drying, this sample was most nearly like normal in its structural organization, with no distortion in spatial relationships. Although the muscle fibres did not shrink, there were long spaces within the fibres, the smallest at the edge of the sample with progressively larger spaces towards the centre, due to the temperature gradients during freezing.

Pre-frozen at −80°. Although the tissue volume was unchanged after freeze-drying, the proportion of muscle fibres and interfibral spaces was altered due to considerable shrinkage of the muscle fibres. The fibres were shrivelled irregularly along their length but without spaces inside. The behaviour suggests that a mixed intra- and inter-cellular freezing had probably determined the morphological pattern of the tissue, i.e., freezing pattern intermediate between that obtained at −150° and −17°.

Pre-frozen at −17°. The dry tissue was characterized by uniform reduction in diameter of muscle fibres and emergence of a new space system bearing no resemblance to endomysial spaces either in size or location. The shrunken fibres were grouped together in small bundles and fibres in the bundles packed without a trace of endomysial space. This morphology appears to result from slow but complete intercellular freezing.

Reconstitution of the freeze-dried materials was assessed and compared by measuring increase in moisture content and of muscle fibre diameter. The over-all high degree of reconstitution of all samples to a moisture level of 84–89% of raw meat and 89–98% recovery of muscle fibre diameter was attributed to absence of protein denaturation, muscle fibre merging, and maintenance of distinct cross-striations. Numerous indications were obtained of a direct quantitative relationship between the space in frozen dried tissue and its capacity to reabsorb water and reconstitute. Samples pre-frozen at −17° had the largest amount of interfibral space and also the greatest degree of recovery of muscle fibre diameter on rehydration and fastest initial water penetration during reconstitution.

Reconstituted meat, pre-frozen at any of the three temperatures, was not readily distinguishable from normal raw muscle tissue.

In freeze-drying, sublimation proceeds from the entire free surface of the sample, and at any given moment the sample consists of two distinct tissues, the completely dry periphery and the raw core. The rate of dehydration is high because of the uninterrupted free passage of water vapour through the porous periphery. In samples subjected to warm-air dehydration, the water passage was blocked as the tissue surface hardened and lost all its endomysial spaces.

When incompletely freeze-dried muscle tissues were dried in a vacuum oven, the dry tissue was unaffected, but in the core the muscle fibres underwent a 30% reduction in diameter and all endomysial spaces disappeared, although merging of adjacent fibres and decreased visibility of cross striations did not occur. Most notably, 'an enormous system of spaces interpolating the dried muscle fibres emerged,' possibly by replacing the endomysial spaces. The tissue rehydrated to a surprisingly high degree, only slightly below the level obtained by completely freeze-dried samples, and far better than ever possible with samples dried without the freeze-drying treatment. The authors suggest that the peripheral frozen-dried tissue acts in some fashion to reduce any serious temperature effect on the core.

Auerbach *et al.* have studied the reconstitution of freeze-dried meat,[26] and have found:

(i) Meat cut against the grain reconstitutes more rapidly and to a higher level than that cut with the grain.

(ii) Rehydration rate and level are influenced by the thickness of the sample: 1-in. sections after 3 hours did not attain water levels achieved by ½-in. sections in 3 min.

(iii) Reconstitution is unaffected by water in the temperature range 22–55°.

(iv) Optimum pH is 7·0.

(v) Reconstitution is more rapid and to a higher level in a vacuum. The product is dark brown in colour probably due to the myoglobin being in a reduced state.

(2) *Accelerated freeze-drying of meat.*—Accelerated freeze-drying (AFD) was developed during a programme of work in which attempts were made to prevent shrinkage of meat during VCD-drying and to produce a porous easily reconstituted product.[27] In this particular instance it was intended to freeze-dry the meat initially so as to enrobe it in a framework of dry tissue, which would thereafter resist volume changes when the heat supply was increased and thawing occurred, in order to promote more rapid drying at higher temperatures. The early results were promising and now several aspects of this procedure have been sufficiently examined to enable the process to be applied successfully to a wide range of animal products (e.g., fish and meat, raw and cooked, in cube, slice, or mince form and also to miscellaneous items such as meat extracts, pre-cooked dishes such as macaroni and cheese, cooked rice, etc.), although it is now doubtful that actual thawing does ever occur.

Fig. 3 illustrates raw pork slices prepared by the AFD and VCD processes. The AFD samples appear identical with freeze-dried meat. (The mesh imprint is derived from the freezing tray on which the fresh meat was laid.) The product is of low density, light in colour, has a very porous surface and a uniformly porous structure throughout the lean tissue. In contrast, the lean tissue of the VCD sample has a dark and glossy surface and shrinks during drying to give a more dense product; the fatty tissue has little water to lose and retains approximately its original volume. These combined factors are typical of VCD raw meat products. Reconstitution is comparatively slow requiring 2-4 hours.

The AFD process can be considered in three stages:

(i) The freezing of the material; (ii) the initial period of freeze-drying; (iii) the completion of the drying cycle using higher plate temperature. The same plant is used for stages (ii) and (iii) as in the VCD process.

(i) Freezing process

The early experiments were carried out using pre-frozen meat, frozen either in a cold room at — 10° or in a blast freezer. This demands additional equipment and factory floor space and to avoid this, freezing of meat by evaporative cooling in the drying cabinet was examined.

Slices of raw meat, laid in the VCD plant with the water circulating through the heating plates at ambient temperatures and with the plates wide open to reduce to a minimum the heat supplied to the meat, froze slowly and irregularly by evaporative cooling. During the freezing process a glossy skin formed over the surface of the meat retarding further evaporation and partially inhibiting freeze-drying. The pellicle is thin but with care can be peeled from the partially dried meat.

If evaporative cooling only slightly exceeds the heat being received from the plates, cooling of the tissue to freezing point will be prolonged and a large amount of water will be evaporated from the aqueous phase. The result is a shrunken tissue with a glossy pellicle (case hardening) which cannot be dried to a porous, rapidly reconstituting product. This was found to be the case in the VCD plant and Fig. 4 illustrates the product.

With improved vacuum, more rapid cooling is obtained, provided migration of water within the meat does not become the limiting factor. Experiments in a small-scale plant showed that water migration becomes the limiting factor in meat sliced with the grain.

Frozen meat undergoes considerable tissue damage with the formation of ice crystals, and on thawing, the phenomenon of drip is observed, due to cell rupture and the breakdown of protein gels in the tissue. Water migration is apparently rapid in thawed tissue which was found to freeze readily by evaporative cooling when held under vacuum. Fig. 5 shows the enhanced cooling effect of thawed tissue. The rapid freezing permits little evaporation from the aqueous phase to occur and the dry product shows little or no evidence of pellicle formation and resembles the AFD meats prepared from pre-frozen meat as can be seen from Fig. 6. This effect is particularly fortunate as some thawing of the frozen meat always occurs when loading a large-scale plant, but almost all quickly refreezes again under vacuum without detriment to the product unless sticking to the tray occurs. If water is provided from an

FIG. 3

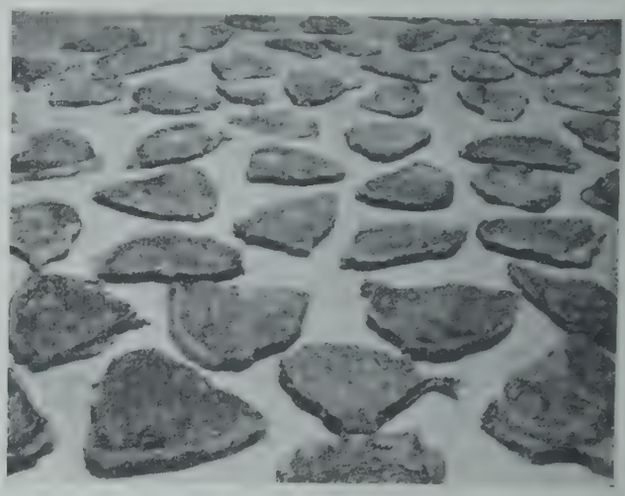

FIG. 4

FIG. 3. *Dehydrated raw pork slices prepared by the VCD and AFD procedures*

The lean tissue of the VCD sample is darker in colour, less porous, shrunken and more dense compared with the AFD sample. The grid marks on the latter sample were derived from the mesh of the freezing trays

FIG. 4. *The product obtained when the dehydration of raw sliced meats is attempted by the AFD process without pre-freezing or any procedure to stimulate freezing by evaporative cooling in the plant*

external source, then rapid freezing of fresh meat should occur and permit subsequent drying to give a typical AFD product. Dipping the meat in water before loading partially achieves this effect, and experiments with the spraying of meat and the trays with water before loading into the plant are very promising. During the cooking process the protein gels of meat are coagulated and water can migrate more readily than in the fresh raw tissue. Hence, when cooked meat is loaded into the plant and vacuum applied, evaporation of water is rapid, leading to swift freezing. Only a small quantity of water is lost prior to freezing and the product prepared by following the AFD procedure is porous and quickly reconstitutes.

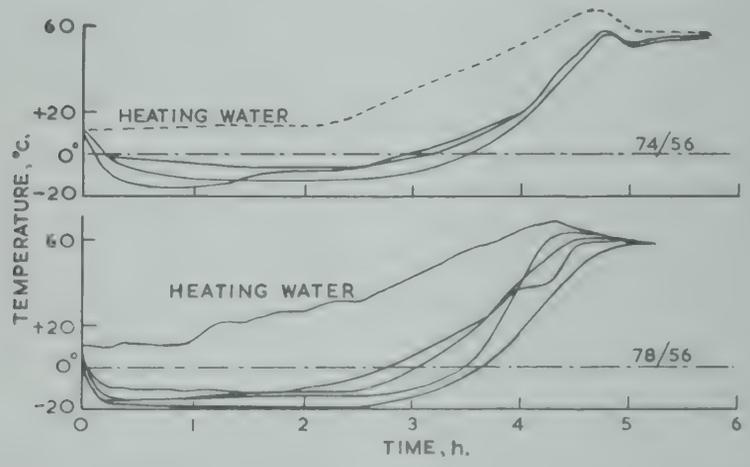

FIG. 5. *Heating water and meat temperatures during the drying of slices of raw meat during evaporative cooling to induce freezing and subsequent drying by the AFD procedure*

Absolute pressure in the cabinet was 0·5 mm. Hg. The thawed meat froze more quickly and maintained a lower temperature during drying, showing that it lost its moisture more readily
Upper curves: chilled meat. Lower curves: meat frozen, sliced and allowed to thaw

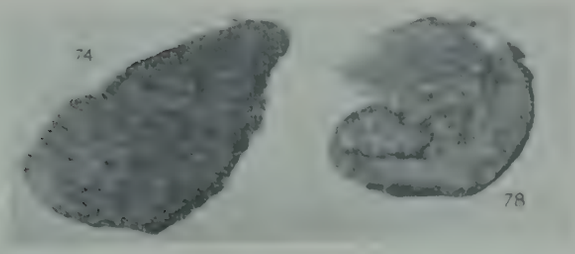

FIG. 6. *Dehydrated raw meats obtained by procedures illustrated in Fig. 5*

Due to rapid and complete freezing of the thawed meat by evaporative cooling, the dry product closely resembles freeze-dried meat. In contrast, the chilled meat, which froze slowly and irregularly, is similar in appearance to VCD meat

If the meat is cooled by refrigeration, the freezing leads to the breakdown of protein gels and denaturation of the proteins. As a general rule, the damage is greatest with slow freezing and particularly with fish a 'cotton-wool' texture can result.

Slow freezing also produces large ice crystals and on sublimation these leave comparatively large voids in the tissue; on the other hand, rapid freezing produces small ice crystals which give rise to small pores in the dry tissue. It was observed that meat frozen slowly, e.g., by holding in a cold room at $-8°$, dried more rapidly than meat quick-frozen in a blast freezer. Because of the variable incidence of fat and connective tissue in meat and the effect of the direction of the grain of the meat which influence the drying, the effect of ice crystal size on the rate of drying was studied using a standard gelatin gel. In such cases it was observed that the slow-frozen gels dried quickly by the AFD process without any shrinkage or distortion, and a moisture content of 6% was obtained after 10 hours with a plate temperature of 40°. The quick-frozen gels dried simultaneously had a fine white porous outer crust, but the central region was one resembling ordinary dried gelatin, i.e., dense and yellow in colour. The dried gels were distorted in shape and had a moisture content of 16%. It is evident that the temperature in the central core rose to thaw the frozen gel and vacuum-drying from the aqueous phase intervened. The rise of temperature at the centre can be explained only by reduced evaporation.

This would be expected from a consideration of the effect of the outer dry crust. Gersh & Stephenson have studied this aspect of the drying process.[28] Heat supplied to ice crystals lying at the interface between the dried shell and the frozen interior causes water molecules to sublime from the free surfaces of these crystals. Such molecules either escape through the dried shell into the drying chamber or return to the interface to be recaptured by an ice crystal. A molecule escaping from an ice crystal may enter the tissue space partially occupied by that ice crystal, and after a number of collisions with the walls it is recaptured by the ice crystal or passes through one of the holes in the walls to a neighbouring space. This space may be another at the interface or it may be one closer to the exterior surface. If the latter, then the molecule will eventually enter a neighbouring space which may again be nearer the exterior surface, and in this way the molecule may eventually reach the surface itself and be removed. In general, a molecule which reaches the surface does so only after making a very large number of collisions within the dried shell. Escaping water molecules will pass through fewer pores and have fewer collisions with their walls if the outer dry crust is composed of coarse rather than fine pores. Consequently, the structure provided by quick freezing would be expected to obstruct the loss of water vapour and reduce the rate of drying.

Pore size also influences the course of reconstitution. Water readily displaces air from the tissue with large pores and gains immediate access into the centre of the meat. Thereafter the walls of the pores quickly imbibe water and the tissue is reconstituted quickly and uniformly throughout. With a dry tissue composed of fine pores, the water is unable to displace all the air, and penetrates only the outer crust. This crust then quickly reconstitutes to form an external gel. The formation of gel retards even further the access of water into the dried meat, so that reconstitution now requires a period of possibly 2 hours or more. Reconstitution can be accelerated by puncturing with a fork, etc., to provide channels for the water to the interior of the meat.

(ii) Initial freeze-drying period

In this stage approximately half the water is removed from the meat, and a dry, porous, light-coloured crust is formed around the outside of the tissue. Very large volumes of water

vapour are evolved, and an easy path of escape from material between its plates into the surrounding cabinet is necessary. Attempts to improve heat transfer by tight plate closure must be avoided as this will stifle evaporation from the surfaces of the meat. There must be adequate channelling within or between the material again to provide a ready escape path for the vapour. Stifling may also occur should thawed meat refreeze tightly on to the tray as moisture vapour will be unable to escape from such areas.

In general, the maintenance of a tissue temperature of $-8°$ has been found to be sufficiently low to ensure true freeze-drying. As the insulating crust of dry tissue builds up on the outside of the drying meat, it becomes possible to increase the plate temperature in order to maintain a rapid evaporation. At this stage any pieces of tissue which are stifled (e.g., abnormally thick pieces and thereby subjected to undue pressure between the plates) will gradually thaw, and dry under conditions similar to VCD drying.

(iii) Completion of the drying cycle

Drying is accelerated by the increased plate temperature applied in the early stages of this part of the process as shown by a marked rise in cabinet pressure. The rise is, however, only to about 2–3 mm. Hg which at equilibrium would indicate a water temperature of $-9°$.

According to thermocouple readings, at this stage the meat is warmer than this, but it is suspected that the recorded temperatures are subject to some error. On examining partially-dried samples, a dry crust has often been found around the thermocouple inside the tissue and probably due to conduction of heat along the thermocouple wire. The dry tissue will not be subject to evaporative cooling, and will therefore register a higher temperature than the surrounding moist material.

The maximum plate temperature employed at any time during this stage is determined by the sensitivity of the material and the avoidance of rendering of fat, etc.

If, during this part of the drying cycle, excessive heat is applied, the resultant product is composed of two clearly defined structures. There is an outer freeze-dried crust, light in colour, porous and easy to reconstitute. The central region is much darker in colour, and built up of fused fibres. This central core is slow to reconstitute and the product when cooked has a processed flavour not apparent in AFD raw meats. A cross-section of such material is shown in Fig. 7. Fig. 8 illustrates the procedure for the AFD accelerated freeze-drying of meat which is described elsewhere.[27]

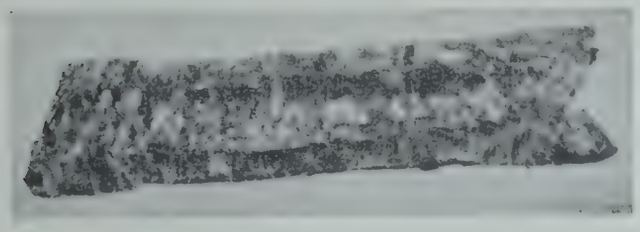

FIG. 7. *Cross-section of a sample of dehydrated raw beef (slice thickness 15 mm.) showing the outer crust of AFD material surrounding a central area of VCD meat*

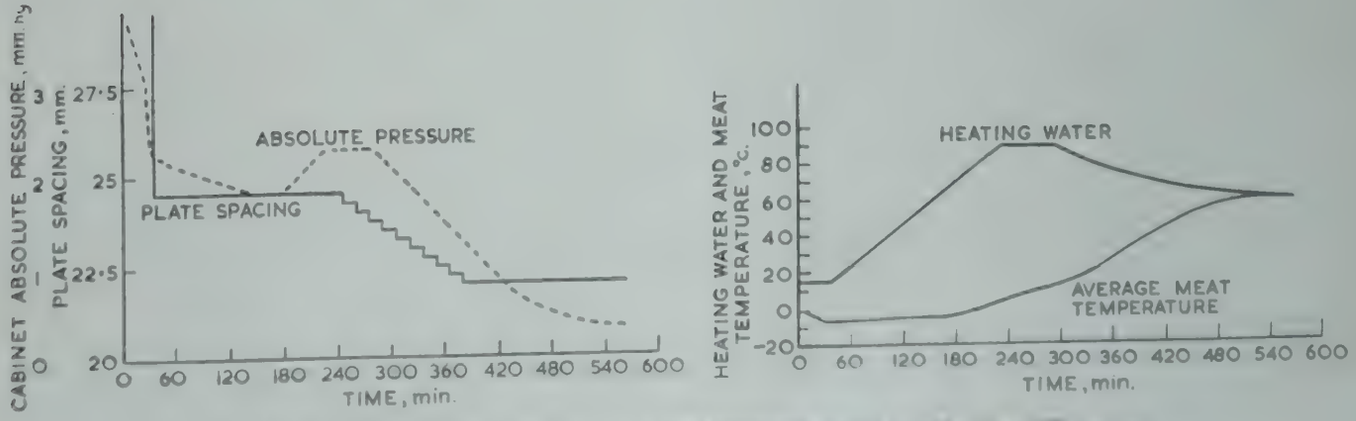

FIG. 8. *Graph illustrating the procedure for drying raw sliced beef by the AFD process* Initial thickness of slices (frozen) 15 mm., thickness of tray and lid 5 mm., tray loading approx. 1 lb. 13 oz./ft.², final moisture content 3%, initial weight 400 lb., final weight 121 lb., 7 trays (8 ft. × 4 ft.)

The composition of the raw material influences the course of the drying. Both the kind of tissue and its structure exert an effect, e.g., the ease of removal of water will vary between fat, connective and lean muscle tissue, and again, their initial water contents will differ very considerably.

Considering first raw meat, the fatty tissue contains only a small amount of water, so that during drying it is subject to only slight evaporative cooling. Its temperature therefore rises more quickly than that of lean tissue and, as little moisture is lost, its structure when dry is not honeycombed so that it is a comparatively good conductor of heat. Adjacent lean tissue will receive more heat during the drying process and, if the amount of fat is large, will tend to produce VCD rather than AFD material. In such circumstances a little rendering of fat may occur to be absorbed by the porous surrounding lean tissue. Complete reconstitution in cold water is thereby hampered but the fat is readily displaced during cooking and the lean reconstitutes at this stage.

Removal of all fat is undesirable as it contains much of the characteristic flavour peculiar to that meat. Indeed, it was observed that, in a reconstitution test on AFD raw lamb chunks, the lean cubes quickly softened while those containing an appreciable amount of fatty tissue were only partially reconstituted. When cooked in this state and submitted to a taste panel the scores showed that incomplete reconstitution of the fatty samples had not adversely affected texture, and also that these samples had the strongest meat flavour.

The cooking process reduces the weight of the meat to approximately 78% of the original raw weight and the greater part of this loss is water. Simultaneously, the proteins lose their gel structure and coagulate, in which form moisture is more readily removed from them. Cooked meat therefore can be dried more quickly and with application of less heat.

As in the dehydration of fresh meat, there is the complication arising from the incidence of excessive adipose tissue. If the heat input is too great during the AFD process, the adipose tissue reaches a temperature at which the fat becomes molten. The fat escapes from the cells damaged by cooking and enrobes the partially dried meat. This results in a rise of the meat temperatures and the final dry products resemble more closely VCD rather than AFD material. Apparently the molten fat impedes the escape of moisture vapour from the interior by blocking the capillaries in the external dry crust of the product and thereby reduces the evaporative cooling so that freeze-drying cannot occur. The rate of drying is very markedly reduced.

When drying fairly lean cooked meat, higher plate temperatures can be employed without experiencing the difficulties with rendered fat. The fatty tissue present in small amounts can be kept cool by the evaporative cooling of the lean meat.

It is therefore desirable that cooked meat dried in a batch should be of similar composition. If much of the meat is very fatty, then cooler plates must be used which will extend the drying time. It has been confirmed that direction of grain has a marked effect on the course of drying. That raw meat cut with the grain loses moisture less readily than meat sliced across the grain was demonstrated by exposing samples 18 mm. thick to a vacuum of $1\frac{1}{2}$ mm. Hg for $\frac{3}{4}$ h. The transverse sections were hard though not completely frozen whereas the longitudinal sections remained plastic. Raw meat moistened externally with water quickly froze under these conditions irrespective of the direction of grain.

For dehydration it is therefore desirable to slice the meat against the grain, but with large-scale production it is impossible to avoid including some longitudinal sections. The latter material is always the slowest to dry, and whereas at the end of the dehydration process the main bulk of the batch may be dry, pieces sliced with the grain retain a flat wet section running through the centre of the piece. Apparently water migrates along muscle fibres more readily than across them. Muscle fibres are very long as compared with their diameter, and water appears to migrate through the actomyosin gel more readily than through membranes of connective tissue.

In an attempt to reduce the incidence of meat cut with the grain, a beef carcass was dissected into muscles rather than cut into joints butcher-fashion before slicing. Muscles with radiating fibres were found so that though meat cut with the grain was reduced, it was not eliminated. As direction of grain is eliminated in minces, these materials are the easiest to dry to a uniform product. Raw minces can be frozen into block form and sliced before drying by the AFD process. The blocks of mince dry uniformly to give a product which reconstitutes

almost instantaneously and coheres sufficiently that, with care, the reconstituted meat can be fried as, e.g., a hamburger steak.

Thin slices

Tough meat, e.g., flank, can be made apparently more tender by cutting into thin slices before eating. In addition, cooked meats are often eaten in thin slices, so that the drying of meat in this form has some interest. If the slices are 3–4 mm. thick and dried as a single layer in the plant, the capacity will be reduced to about one-fifth and though drying of this thin material will be more rapid, it will be insufficient to compensate for the reduced capacity. Slices of both raw and cooked meats have therefore been dried stacked on the trays in piles 4–5 slices thick. Drying by the AFD process provides a uniform product throughout the piles. The slices dry without shrinkage, and give an easily reconstituting product. This would suggest that the conditions employed in the AFD process do in fact freeze-dry the materials throughout, and not just simply on the outer crust.

Hunt & Matheson have studied the effect of denaturation by the AFD process on actomyosin in fish and beef muscle,[29] this being chosen as it is the major protein in muscle tissue.[30] In addition, it is rather labile and its survival during processing would indicate that many other proteins would also remain undamaged.

Actomyosin behaves as an enzyme and can hydrolyse adenosine triphosphate (ATP) to adenosine diphosphate (ADP). This provides a convenient means of following the denaturation of actomyosin by measuring the loss of ATP-ase activity. Other properties affected by denaturation are solubility in 0·5M-potassium or sodium chloride solutions and contraction of muscle fibres in presence of ATP. These also were examined.

It was observed that AFD raw beef retains more than half the ATP-ase activity of the fresh, and a similar result was obtained for cod. Solubility measurements were confined to cod and the results suggest that all the actomyosin was denatured by the dehydration treatment. Muscle fibres from AFD beef were found to be contractile in the presence of ATP although the fibres contracted to a lesser extent and at a slightly slower rate than the fresh.

It is apparent that there is some damage to the actomyosin caused by the AFD process but this does not appear seriously to affect the products.

Canadian freeze-drying process

Workers in Canada at the Defence Research Medical Laboratories have been attempting to reduce the drying time required for the freeze-drying of meats. They soon concluded that the limiting factor was the transfer of heat to the evaporating ice surface which gradually recedes further and further into the tissue. This problem was overcome by impaling the meat on metal spikes long enough to extend right throughout the meat and which effectively conducted the heat into the centre of the drying tissue.[31] The spikes, which are up to $\frac{1}{8}$-in. diam. and about $\frac{1}{2}$ in. apart, enter from each side and are staggered so that the maximum thickness of meat between heating surfaces is only $\frac{1}{4}$ in.

The plant used was a conventional freeze-drying chamber with the meat laid between heating plates fitted with the spikes of aluminium or stainless steel. By this procedure raw meat steaks $\frac{1}{2}$–1-in. thick have been dried in $2\frac{1}{2}$–$4\frac{1}{2}$ hours and roast-size pieces $2\frac{1}{2}$ lb. in weight in 5–8 hours. Reconstitution takes less than 30 minutes for $2\frac{1}{2}$ lb. of roast and 5 minutes for a steak in cold water. During reconstitution the holes in the dried meat close up and are not apparent after cooking.

Possibly equally important in this procedure to the good heat transfer achieved by the spikes, is the avoidance of any stifling by application of even light plate pressure such as is necessary using the VCD equipment. With the rapid drying time achieved by this process, the volume of water vapour removed at a pressure in the region of 1 mm. Hg is very large and if escape were restricted in any way the heat input would have to be reduced to prevent thawing, and the drying time would be extended.

Because of the rapid evolution of water vapour achieved by this process a very efficient system must be used to remove it from the plant.

Acknowledgment

It is a pleasure to acknowledge the assistance of Mr. and Mrs. Cox in the study of the VCD and AFD processes.

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Discussion

Mr. J. F. Hearne: In the reconstitution of active dry yeast there is said to be an optimum temperature of about 43°. The argument is that, at this temperature, reconstitution of the cell wall is rapid and leaching of cell contents at a minimum. In AFD meat the texture is very porous and wetting can be very quick. Is there any analogy between reconstitution of yeast and AFD meat? Could Mr. Rolfe say whether there is an optimum temperature for reconstitution of AFD meat?

Mr. Rolfe: Auerbach and co-workers in U.S.A. have studied this aspect and report that reconstitution is unaffected by water in the temperature range 22–55°. I have not studied this aspect systematically and can only say that hot water, i.e., near boiling, has an adverse effect on dehydrated raw meat and the use of cold water is recommended.

Mr. T. W. G. Rowe: In reply to a question to Mr. Rolfe concerning puff drying, we have had some experience of the puff drying of orange juice which must behave in a similar manner to blackcurrant juice. As Dr. Gane has said, the freezing point of concentrates is low so that the question of their being freeze-dried does not really arise. This being the case they can be vacuum pre-concentrated and then puff dried.

We heated our shelves to about 80° and pumped the vapour directly with an air-ballasted rotary pump. The rapid formation of bubbles about ½-in. in diameter was followed by slow-forming bubbles up to 2-in. in diameter. The temperature of the product could not be measured because it did not remain in contact with the shelf. I agree that the puffing is difficult to control, and the rate of heating has to be balanced against that of pumping. Our product, when reconstituted, had suffered some loss of flavour but it compared favourably with the original. I am told, however, that the public prefers the taste of preservative which it has grown to like.

In reply to a question concerning dielectric heating equipment, I have been in correspondence with the company in the United States which makes such equipment. They claim an economy over conventional methods when they freeze-dry on a large scale, but they do not say whether investment and depreciation costs, as well as operating costs, are taken into consideration.

I understand that high vacuum involving, presumably, the use of low-temperature condensers and diffusion pumps is needed to prevent gas discharges from occurring.

DEHYDRATION OF VEGETABLES IN MULTI-STAGE CROSS-FLOW SYSTEMS

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(*Ministry of Agriculture, Fisheries and Food, Experimental Factory, Aberdeen*)

Dehydration of vegetables in tunnels with longitudinal air flow has certain disadvantages, in particular, that each succeeding batch is affected by those upstream. As alternatives to tunnels, three- and four-stage systems, employing counter-current air flow with interstage reheating to graded temperatures, have been examined. The three-stage system showed definite advantages over the twin tunnel system used during the Second World War, and the four-stage system was superior to the three-stage. The effect of operating variables is discussed in some detail.

Introduction

Many drying systems have been proposed for the dehydration of vegetables, but no general agreement has been reached, nor is yet in sight, as to which system produces the best products with the greatest economy.

Systems operating at a single, relatively low temperature throughout the period of drying have been advocated; in others, preference is given to high temperatures and more rapid drying in the early stages. Ede & Hales[1] considered that vegetables dried as quickly as possible (provided that conditions were not so severe as to cause heat damage) gave a better product than those dried slowly.

In Britain, the tendency has been to seek a general-purpose drying system—viz., one which will handle a wide range of vegetables rather than one specifically tailored for one commodity; even so, through-draught conveyor dryers, over-draught and through-draught cabinet dryers, and over-draught tunnel dryers have found application, and in particular, during the Second World War a great deal of experience was gained with the last type.

More recently, experience has been obtained at this factory of the use of three- and four-stage cabinet systems, and the main purpose of this contribution is to outline and discuss the results obtained. The approach has been practical rather than fundamental, the experiments having been carried out on the factory scale, wherein lies the particular value of this work. It is not proposed to discuss in detail the physics of drying vegetables as this has been well covered by Ede & Hales,[1] by Scott[2] and in papers presented to this conference.

Basic considerations in the drying of vegetables

(i) Scalded vegetables contain 80–95% water, which is a much greater proportion than occurs in many other substances which are dried commercially (e.g., chemicals, dyes, clays), and is comparable with that in milk, i.e., about 87% water.

(ii) Except in leafy parts of green vegetables, the natural size of piece (e.g., carrot) is much too thick to allow uniform and rapid evaporation from the whole of the tissue. (It is usual to cut the material so that the thickness of piece is a uniform $\frac{1}{8}$ in. or $\frac{3}{16}$ in.; dimensions in other directions are less important, but a so-called ' standard ' width of strip of $\frac{5}{16}$ in. has been adopted for past Services contracts, the strips being of random lengths.)

(iii) Most foodstuffs suffer heat damage during drying if they are held at temperatures above about 160°F for protracted periods, especially if their water ratio has fallen below about 0·25 (i.e., moisture content of 20%).

(iv) In the early stages of drying, the rate of evaporation is governed by the drying power of the air.

(v) In the early stages of drying, evaporative cooling maintains the temperature of the vegetable at or near the wet-bulb temperature of the circulating air and high dry-bulb temperatures are therefore permissible if the wet-bulb temperature is maintained at a low level.

(vi) In the later stages of drying, evaporation becomes progressively slower and increasingly governed by the rate at which water can diffuse to the surface of the material.

(vii) In the later stages of drying, the reduced evaporation rate allows the temperature of the material to rise, so that it gradually approaches, and ultimately reaches, the dry-bulb temperature of the circulating air; this enforces the use of lower dry-bulb temperatures in these stages.

Conditions in tunnel dryers

Ede & Hales[1] have described the conditions governing over-draught drying on trays, and Scott,[2] van Arsdel[3] and Kilpatrick *et al.*[4] have described the conditions in concurrent flow and counterflow dehydration tunnels.

During World War II the British Ministry of Food set up a number of vegetable dehydration factories which have been described in ' Vegetable Dehydration.'[5] The drying system was a two-stage over-draught tunnel dryer. In the first stage (the ' wet tunnel ') the wet material, spread on wire mesh trays and loaded into trucks, was first placed near the discharge side of a fan blowing hot air along the tunnel. At regular intervals of time, further trucks were inserted near the fan, those already in the dryer being moved progressively further away from it. The air flow in this stage was thus concurrent with the movement of the trucks. When these reached the end of the first stage (i.e., half-way through the drying cycle) they were transferred to the second stage (the ' dry tunnel '), which they entered at the end remote from the fan, so that in this stage the airflow was counter-current.

Air entered the dryer upstream of the fan in the counterflow tunnel; the amount entering was only a fraction of the amount which was handled by the fan, since after passing the trays the air was led back by ducting to the inlet of the fan, to be mixed with the incoming fresh air and heated before being recirculated over the trays. A proportion of the returning air was directed into the ducting of the concurrent-flow tunnel, which then operated similarly to the counter-flow tunnel except that a proportion of the moist air was discharged outside the factory after passing over the trays. Relatively high inlet temperatures could be used in the concurrent flow tunnel and temperatures not exceeding 160°F in the counterflow tunnel. Evaporative cooling reduced the temperature of the air along the concurrent-flow tunnel so that heat damage to the drier material near the exit end did not occur unless temperatures at the inlet end were raised unduly.

The system, however, has the drawback that the conditions at either end of the concurrent-flow tunnel cannot be altered independently, e.g., the temperature at the initial stage is limited by the temperature which can be withstood by the material at the exit: the humidity at the exit is affected by factors, e.g., tray load, which affect the humidity at the inlet, and so on. The normal conditions of operation (for potato) were: wet tunnel inlet, 210–215°F dry bulb; exhaust end, 145°F dry bulb, 115°F wet bulb; dry tunnel inlet, 160°F dry bulb. The tunnel held six or seven ' batches ' inserted at 30-min. intervals. The water ratio of the material leaving the wet tunnel was approximately 0·4 (30% moisture) after 3–3½ hours' drying.[5] There appear to be no published records of temperatures at various points along the tunnel, but observations made in dehydration factories during the Second World War, and published figures based on calculations by Kilpatrick *et al.*,[4] indicated that the conditions were of the type shown in Figs. 1 and 2 when the tunnel was working with normal loading. This suggests that the temperature of the vegetable was being held at a rather dangerously high level towards the end of the first tunnel, and evaporation had dropped to a low rate. If, in an attempt to increase production, the tray loading is increased, the resulting increase in humidity reduces evaporation at an earlier stage in the tunnel and prolongs the period for which the partially dry vegetable is held at a relatively high temperature, thus increasing the danger of heat damage. This is an ever-present danger in production factories even today.

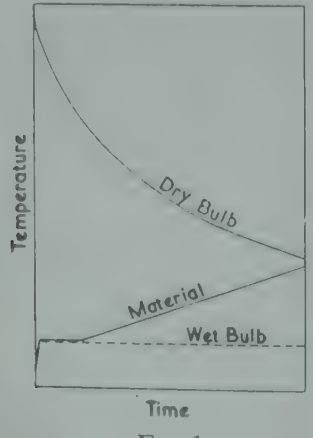

FIG. 1

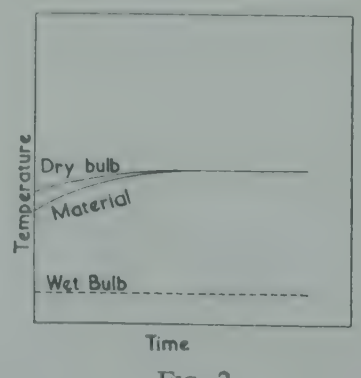

FIG. 2

FIG. 1. *Temperature in concurrent flow tunnel*
FIG. 2. *Temperature in counterflow tunnel*

Three-stage drying

To overcome these drawbacks it seemed logical to divide the first stage and make a three-stage system. Scott[2] has suggested that high drying rates and reasonable thermal efficiency would be obtained with counterflow drying in stages with interstage re-heating to graded temperatures, the inlet air being supplied at a safe temperature for the finished product and then re-heated progressively to the maximum temperature which the moister material can withstand.

This principle was put into operation at Aberdeen, with a three-stage system (Figs. 3–5), consisting of three cabinets with cross-flow air circulation. Air is taken into the third cabinet (i.e., the cabinet in which the final drying takes place), heated and passed over the vegetable; from this cabinet, air is passed to the second cabinet, where its temperature is raised to a higher level before circulation over the vegetable; from the second cabinet the air is passed to the first cabinet and re-heated to a still higher level before being passed over the wettest material and then vented.

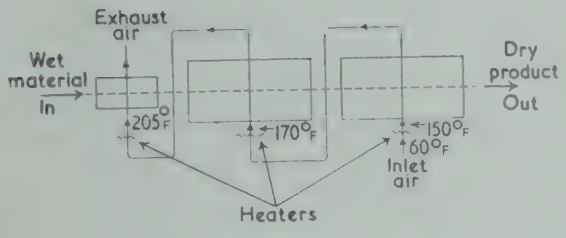

FIG. 3

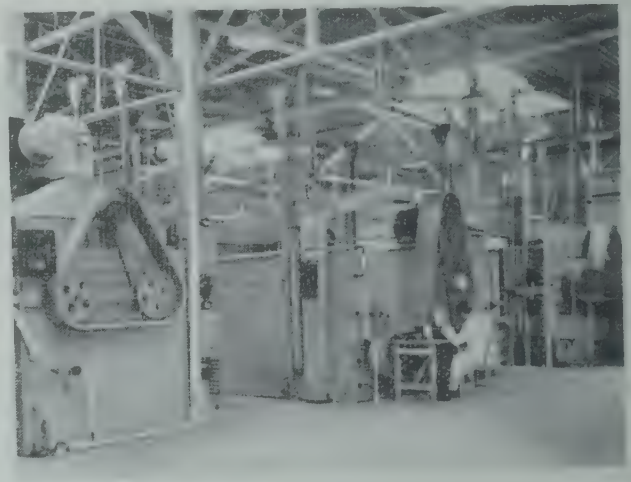

FIG. 4

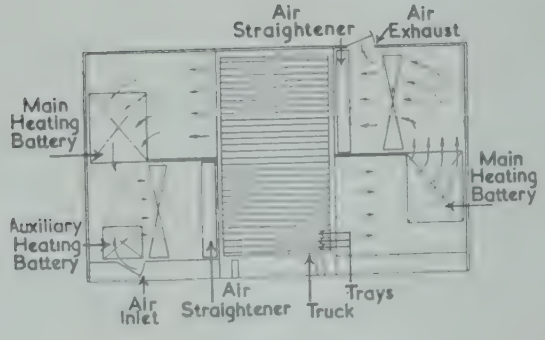

FIG.

FIG. 3. *Diagram of three-stage drying system*

FIG. 4. *The three-stage dryer at the Experimental Factory* (Crown Copyright)

FIG. 5. *Diagrammatic section of first cabinet of three-stage drying system (also used as second cabinet of four-stage system)*

Air-flow in the first cabinet is about 850 linear ft. min., in the second and third cabinets about 750 ft. min. The principal duty of the fans is to circulate the air over the vegetable, but the vented air connections are so sited relative to these fans as to assist the action of a separate extraction fan in the exhaust from the first stage, which serves to draw the air through the system. Control of the humidity in each cabinet can be obtained both by the recirculation dampers and by bleeding fresh air into the interconnecting ducting. In practice it has been found unnecessary to bleed in any air, and the recirculation setting is such that in normal operation

the amount of air circulating in the first cabinet is four to five times the amount entering and leaving; in the other cabinets the ratio of circulating to discharged air is higher.

The first cabinet is smaller than the others and holds two trolleys each with 56 trays of area $3\frac{1}{2}$ sq. ft.; one pair of trolleys forms one 'batch.' The second and third cabinets each hold four batches. For continuous operation, therefore, the total drying time is 9 times the period of insertion between successive batches: for example, if the insertion period is 30 min., the total drying time is $4\frac{1}{2}$ h. (less the few minutes involved in transferring the trolleys from cabinet to cabinet).

At the start of experiments on potatoes, previous experience with tunnel dryers led to the adoption of the following conditions, which were expected to give reasonably satisfactory results with potato strips $\frac{3}{16} \times \frac{5}{16}$ in. cross-section.

Stage	Time, min.	Dry-bulb temp., °F	Wet-bulb temp., °F
1	30	205	135
2	120	170	125
3	120	150	90

Tray load 1·43 lb./sq. ft. (=5lb. per tray)

The temperature quoted for Stage 1 was the maximum which could be maintained in the equipment available.

With these arbitrary conditions as a basis for experiment, several aspects of dryer operation have been examined in some detail. Full experimental results have been presented elsewhere,[6a–d] and some of these are briefly summarized in the tables; the following paragraphs will be confined to a discussion of the findings.

Temperature of the vegetable during drying

Thermocouple measurements of the temperatures inside potato strips $\frac{3}{16} \times \frac{5}{16}$ in. cross-section, located near the centres of trays, showed that during the first stage of drying, the vegetable remains at the wet-bulb temperature of the circulating air for most of the period (actually about 25 min.). This is in contrast to the findings of Ede & Hales[1] with single strips of potato, who found no lag at the wet-bulb temperature, but a steady rise to the dry-bulb temperature, but is more nearly in agreement with the calculations of Kilpatrick *et al.*[4]

After this period of lag, the temperature of the strips on the tray begins to rise quite sharply, this change in behaviour taking place when the mass of vegetable as a whole has reached a water ratio between 2·5 and 3·0. In the second stage, the dry-bulb temperature of the vegetable continues to climb away from the wet-bulb temperature and it is within 1°F of the dry-bulb temperature after 1 to $1\frac{1}{2}$ hours in this stage. For the remainder of the drying period there is no detectable difference between the temperature of the vegetable and the dry-bulb temperature of the circulating air[7] (Fig. 6). In the observation of the writers it has frequently occurred that heat damage is first noticed in the latter part of the second stage, at a water ratio of about 0·2.[7] This fact, together with the knowledge that the temperature in the vegetable itself is high at this stage, leads to the opinion that this is the dangerous period so far as heat damage is

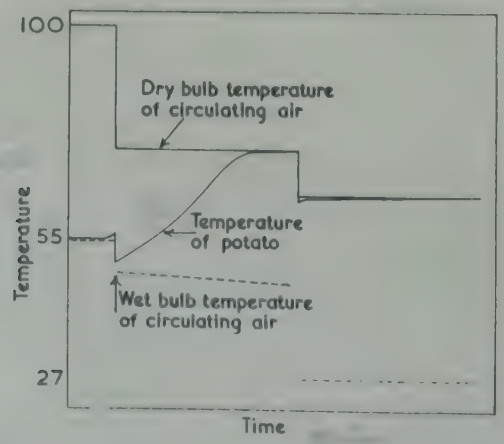

FIG. 6. *Temperatures in three-stage hot-air dryer (potato strips $\frac{3}{16} \times \frac{5}{16}$ in. cross section)*

concerned; lowering the stage-2 dry-bulb temperature from the proposed 170° to 165°F greatly reduces this damage.

The rapidity with which the temperature of the foodstuff reaches the dry-bulb temperature in the relatively long second stage of this system suggested that a better design would be to have a shorter second stage (holding say two batches) and a longer third stage, holding say six batches, or, better, to have a four-stage system with short first and second stages, a longer third stage and an even longer fourth stage. (This has in fact been done, and will be described later.)

Effect of tray load

Ede & Hales[1] found, and abundant experience of tunnel drying has confirmed, that in practice the maximum load of wet vegetables that could be handled satisfactorily by over-draught drying was about 1½ lb./sq. ft., unless the load on each tray was respread at some point during the drying operation. Higher loadings brought about a blanketing effect (especially with leafy vegetables), and the unavoidable unevennesses of tray spreading were far more liable to lead to wet patches in the product as loads increased. More rapid drying in the early stages was reported for lighter loads; the practical problem is whether the more rapid drying of lighter loads would allow as rapid or more rapid output of a dehydrated product of good quality.

Experiments with potato strips, carrot strips and cabbage, within the tray load range, 0·9 to 1·5 lb./sq. ft., showed that reducing the tray load did lead to a substantially greater degree of drying in the early stages if a 30-min. insertion cycle were used, but the differences were small (e.g., in the case of carrot) or absent (e.g., potato) when a 40-min. cycle was employed. Even with the shorter cycle, by the end of the third stage the differences had virtually disappeared, except for the very lightest loads of 0·9 lb./sq. ft. (Tables I and II).

Table I

Effect of tray load on rate of drying
(Potato strips $\frac{3}{8}$ × $\frac{5}{16}$ in. cross-section)

Tray load, lb./sq. ft.	Water ratio, lb. water/lb. dry matter			
	Initially	After stage 1	After stage 2	After stage 3
1·0	5·41	2·10	0·071	0·055
1·2	5·10	2·60	0·098	0·056
1·5	5·25	3·38	0·205	0·058
Drying conditions: Stage 1: 30 min. at 205°F DB; 135°F WB Stage 2: 120 min. at 170°F DB; 125°F WB Stage 3: 120 min. at 150°F DB; 90°F WB				
1·25	5·61	1·96	0·054	0·038
1·5	6·25	2·59	0·052	0·038
1·6	6·50	2·89	0·063	0·044
Drying conditions: Stage 1: 40 min. at 205°F DB; 135°F WB Stage 2: 160 min. at 170°F DB; 125°F WB Stage 3: 160 min. at 160°F DB; 90°F WB				

DB = Dry-bulb WB = Wet-bulb

Table II

Effect of tray load on rate of drying
(Carrot strips $\frac{3}{16}$ × $\frac{5}{16}$ in. cross-section)

Tray load lb./sq. ft.	Water ratio, lb. water/lb. dry matter			
	Initially	After stage 1	After stage 2	After stage 3
1·42	9·5	5·49	0·128	0·063
1·29	9·9	5·30	0·101	0·063
0·90	9·7	2·66	0·090	0·053
Drying conditions: Stage 1: 30 min. at 205°F DB; 135°F WB Stage 2: 140 min. at 175°F DB; 125°F WB Stage 3: 140 min. at 150°F DB; 90°F WB				

The actual maximum loads which could be handled in practice were, as expected, limited by the incidence of wet patches and were eventually standardized at 5 lb. per tray (1·43 lb./sq. ft.) for root vegetables and 4 lb. per tray (1·14 lb. sq. ft.) for water-scalded leafy vegetables, but 4½ lb per tray (1·29 lb. sq. ft.) for steam-scalded leafy vegetables. This latter difference is because tray spreading is done *before* steam scalding, and leafy vegetables are then easily spread into a loose mass; when they are spread *after* water scalding they are soggy and limp and tend to form mats which persist as wet patches at the end of the normal drying period. It may be noted that tray loads containing the same weight of moisture in potato, carrot, and cabbage would carry vegetable weights in the approximate ratio 5·0 : 4·6 : 4·3 because of the different dry matter content of the three vegetables.

With regard to any possible reduction in drying time which might be obtained by using smaller tray loads, the case of potato may be considered. When this vegetable was dried in the form of strips $\frac{3}{32} \times \frac{5}{16}$ in., with a 30-min. insertion cycle, the heaviest load (1·5 lb./sq. ft.) reached a water ratio of 0·058 after 4½ hours. Assume that this is the desired final moisture content; it appears likely from Table I that material loaded at 1 lb. sq. ft. might reach that moisture content after perhaps 1 hour in the third stage—i.e., after 3½ hours' drying. It would not, of course, increase the throughput of the existing plant to reduce the third stage to 1 hour; a reduction in drying time would necessitate a reduction in the interval between insertion of successive batches, and on a 3½-hour total drying time this would be about 23 minutes, giving 23 minutes in stage 1 and 92 minutes in each of stages 2 and 3. (In practice, owing to the reduction in evaporation consequent upon the reduced periods in stages 1 and 2, a greater load of moisture would be entering stage 3, and 92 minutes at this stage might be insufficient; the 3½-hour period will, however, be retained as a basis for argument.) There is, therefore, a reduction in tray load of 33·3% and a reduction in drying time of 22·2%. The figures for carrot (Table II) indicate a similar state of affairs. Obviously, therefore, reduction in tray load would involve a loss of throughput, and the desirability (subject to the limitations noted at the beginning of this section) of using the maximum possible tray load is clear.

Effect of changes in initial period of drying

About 95% of the total evaporation in the dryers occurs in the first and second stages. Increasing the drying period by 5 or 10 minutes in the first stage leads to a corresponding increase in the amount of water evaporated during this period, and an equivalent decrease in the water evaporated during the second stage, provided the drying time in the second stage remains constant (Table III). Intermediate weighings of trucks have shown that most of the work in the second stage is done within the first hour, and the implication again is that a shorter second stage would lead to a better balanced and more efficient system.

Table III

Effect of varying period of drying at different temperatures

(Potato strips $\frac{3}{32} \times \frac{5}{16}$ in.)

Water ratio initially	Period in stage 1, min.	Water ratio after stage 1	Period in stage 2, min.	Water ratio after stage 2	Period in stage 3, min.	Water ratio after stage 3
5·29	30	3·02	120	0·114	240	0·055
5·13	35	2·10	120	0·091	240	0·056
5·13	40	1·99	120	0·086	240	0·058
5·17	30	2·45	120	0·122	360	0·055
5·17	35	2·30	120	0·115	360	0·049
5·17	40	1·58	120	0·078	360	0·047

Drying conditions: Stage 1: 205°F DB; 135°F WB
Stage 2: 170°F DB; 125°F WB
Stage 3: 150°F DB; 90°F WB

Tray load = 1·4 lb./sq. ft.
(water ratio = lb. water/lb. dry matter)

Effect of thickness of piece

It is well established[1, 3] that material cut more thinly will dry more rapidly, or in a given time to lower moisture contents, than thicker material. The practical effects of cutting potato and carrot strips to different thicknesses have been studied in the three-stage Aberdeen dryers.

Three sizes of strip have been used of cross-section $\frac{3}{16} \times \frac{5}{16}$ in., $\frac{1}{8} \times \frac{5}{16}$ in. and $\frac{3}{32} \times \frac{5}{16}$ in. The most thinly cut material has the highest water content when it enters the cabinets, owing to the greater area of surfaces retaining water from the scalding process. After stage 1 this difference has been more or less eliminated and in stage 2 the loss in moisture is progressively greater with the reduction in thickness of the strip. This difference is maintained in stage 3 (Tables IV and V show typical figures for potatoes and carrots). The small difference at the end of stage 1 is presumably because nearly all the evaporation in this stage is of moisture from the surface and the outer layers of the strips (as the temperature of the strips during this stage suggests); in the early part of stage 2, however, the greater surface area of the thin strips results in a higher evaporation rate. The lower final moisture contents of thinner strips after a definite period of drying are a direct result of the shorter diffusion path; this effect is of major importance in determining the ultimate moisture content of the product attainable in practice. The difficulty of reducing the water ratio of strips $\frac{3}{16}$ in. thick to less than about 0·065 (moisture content = 6·2%), even with prolonged third stage drying, is considerable; the rapidity with which material of half this thickness can be brought to water ratios of below 0·055 (moisture content = 5·2%) is striking. In deciding, however, on what is the best thickness of strip for general use, various other factors have to be considered. The thinner strips, by virtue partly of the greater leaching they have suffered, particularly during water scalding, and partly because during drying they pass more quickly through the dangerous 20–10% moisture content zone, can stand higher temperatures during the second stage of dehydration, with consequent added acceleration of drying. Their low final moisture content and greater extent of leaching both increase their resistance to browning during subsequent storage. They require no soaking before cooking, but potato strips $\frac{3}{32}$ in. thick cook so rapidly that they easily reduce to a mush when handled on a large scale, and both potato and carrot strips of this dimension, even if properly cooked, are weak in flavour and so thin and translucent as to be unattractive. A strip thickness of $\frac{1}{8}$ in. seems to be a satisfactory compromise for potatoes and may prove to be for carrots.

Table IV

Effect of strip thickness on rate of drying
(Potato)

Strip dimensions, in.	Water ratio (lb. water/lb. dry matter)			
	Initially	After stage 1	After stage 2	After stage 3
$\frac{3}{16} \times \frac{5}{16}$	4·43	2·47	0·23	0·069
$\frac{1}{8} \times \frac{5}{16}$	4·88	2·71	0·21	0·056
$\frac{3}{32} \times \frac{5}{16}$	5·17	2·46	0·12	0·054

Drying conditions: Stage 1: 30 min. at 205°F DB; 135°F WB
Stage 2: 120 min. at 170°F DB; 125°F WB
Stage 3: 360 min. at 150°F DB; 90°F WB
Tray load = 1·4 lb./sq. ft.

Table V

Effect of strip thickness on rate of drying
(Carrot)

Strip dimensions, in.	Water ratio (lb. water/lb. dry matter)			
	Initially	After stage 1	After stage 2	After stage 3
$\frac{3}{16} \times \frac{5}{16}$	9·5*	5·25	0·18*	0·065*
$\frac{3}{32} \times \frac{5}{16}$	10·1*	5·75	0·13*	0·051*

Drying conditions: Stage 1: 30 min. at 210°F DB; 135°F WB
Stage 2: 140 min. at 170°F DB; 125°F WB
Stage 3: 140 min. at 150°F DB; 90°F WB
Tray load = 1·3 lb./sq. ft.
*Members of pair significantly different ($p = 0·05$)

Time required in third stage

It has already been seen that, within reasonable limits, variation in tray load and the period of drying in the early stages has little effect on the final moisture contents of strips of the same thickness. All the drying curves, divergent though they may be in the early stages, eventually coincide during the third stage of drying, when the rate of diffusion of water from the centre of the piece to the outer evaporative surfaces is the factor controlling the drying rate. Drying is extremely slow at this stage and, with other conditions the same, prolonging the drying time at 150°F from 2 hours to 6 hours for potato strips $\frac{3}{16} \times \frac{5}{16}$ in. has only reduced the water ratio from 0·096 to 0·070 (moisture content 8·7% and 6·5% respectively). Corresponding figures for strips $\frac{3}{32} \times \frac{5}{16}$ in. are 0·064 (= 6·0%) and 0·049 (= 4·7%) (Table VI). Cross-flow tray dryers are not ideal for these long drying periods; bin drying or deep tray through-draught dryers are undoubtedly better (for reasons to be stated later), and a deep tray dryer has been installed as part of the four-stage system described below.

Table VI

Effect of prolonging drying in third stage

(Potato strips)

Strip dimensions, in.	Period in third stage, min.	Final moisture content: Expressed as lb. water/lb. dry matter (water ratio)	Final moisture content: Expressed as % of wt. of product
$\frac{3}{16} \times \frac{5}{16}$	120	0·096	8·7
	150	0·090	8·2
	240	0·080	7·4
	360	0·070	6·5
$\frac{1}{8} \times \frac{5}{16}$	180	0·059	5·6
	240	0·056	5·3
$\frac{3}{32} \times \frac{5}{16}$	120	0·064	6·0
	150	0·063	5·9
	240	0·055	5·2
	360	0·049	4·7

Drying conditions: Stage 1: 30 min. at 205°F DB; 135°F WB
Stage 2: 120 min. at 170°F DB; 125°F WB
Stage 3: variable at 150°F DB; 90°F WB
Tray load = 1·43 lb./sq. ft.

Four-stage drying

In this system, as employed at Aberdeen, there is a short first stage (holding one batch of vegetables), a short second stage (one batch), a longer third stage (four batches) and a fourth stage as long as the first three stages together. If the system is working continuously, the drying time is twelve times the insertion period (6 hours if the period between insertion of successive batches is 30 minutes). The first three stages are interconnected cross-flow over-draught cabinets, the last stage may be of the same type or it may be a deep tray finishing dryer with through-draught air flow. In the unit at Aberdeen each tray in this dryer holds the partially dry product from one trolley from the cross-flow third stage.

The first-stage cabinet is capable of operating at higher temperature conditions than that of the three-stage system, and as the result of numerous experimental trials the following operating conditions have been adopted as standard for root vegetables:

Stage	Time, min.	Dry-bulb temp., °F	Wet-bulb temp., °F
1	30	230	125
2	30	175	120
3	120	155	115–105
4	180	145	90–80 in cross-flow dryer; 80 in through-flow dryer

Tray load 1·43 lb. per square foot (5 lb./tray).

Under these conditions, strips of potato or carrot, $\frac{1}{8} \times \frac{5}{16}$ in. cross-section, are brought to an average water ratio of about 0·055 (moisture content 5·2%) and strips $\frac{3}{16} \times \frac{5}{16}$ in. cross-section to 0·066 (moisture content 6·3%) without any visible heat damage even in very sensitive material such as steam-scalded potato of high reducing sugar contents (up to 6% dry basis).

The rate of drying in the earlier stages is rather more rapid than that in the three-stage drying system previously described; this is partly due to the higher dry-bulb temperature and greater wet-bulb depression in the first stage, and partly to the higher temperatures permissible in the short second stage (Fig. 7).

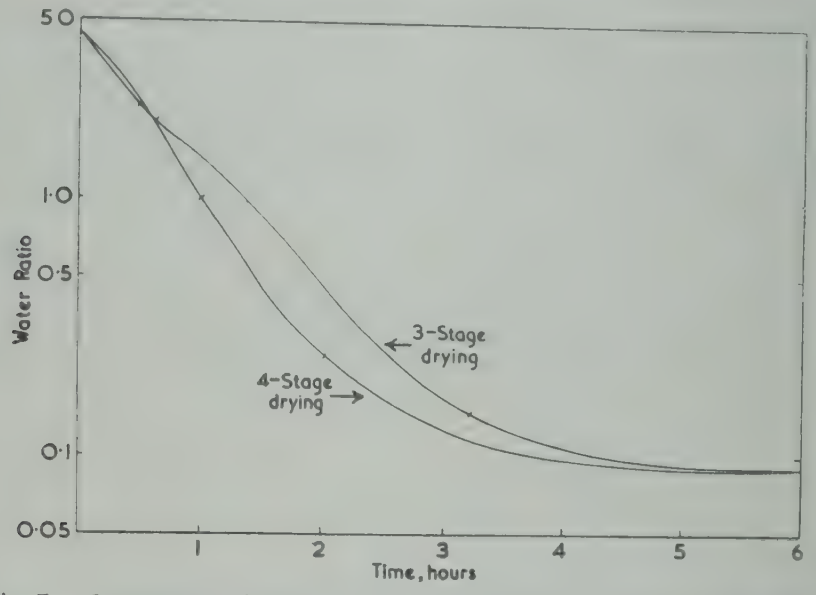

Fig. 7. *Comparison of water ratios (potato strips $\frac{3}{16} \times \frac{5}{16}$ in.)—three-stage and four-stage drying*

If relatively high moisture contents are acceptable, e.g., water ratio 0·06 to 0·07 in strips $\frac{1}{8}$ in. thick, drying can be stopped after 3 hours, but if the water ratio is to be reduced to the order of 0·05, even with strips as thin as this, a further 3 hours' drying at 145°F is necessary. Raising the finishing temperature to 150°F reduces the finishing time by about an hour, but increases the danger of heat damage should the material be particularly sensitive. To obtain moisture contents of this order in the three-stage system, a total drying time of $6\frac{1}{2}$ hours was required, and the four-stage system leads to a small reduction in total drying time (30 min.), compared with the three-stage system, but, by eliminating the dangerously high temperatures of stage 2 in the latter, it greatly reduces the danger of browning during drying.

The finishing stage may be, as mentioned above, either a cross-flow dryer, or a deep tray through-draught dryer. The latter has many advantages; it occupies one-third of the floor space of the former; it employs a single fan and heater battery instead of eight fans and four heater batteries; the power consumption is approximately 2 kW per hour, and steam consumption approximately 75 lb. per hour, compared with $7\frac{1}{2}$ kw and 100 lb. for similar amounts of evaporation. One drawback, however, is that the partially dry product has to be transferred from the trays of the cross-flow dryer to the deep trays of the finishing dryer, so involving additional handling.

Opinions differ as to the best method of drying beyond the region of water ratio about 0·1. In British practice, fairly rapid drying has been favoured and finishing temperatures of as much as 160 F are often used, in spite of the attendant danger of causing heat damage to the product. In the U.S.A., on the other hand, prolonged drying, 24 to 48 hours, at 115–125°F is often preferred, deep bins with through-draught drying being employed for this purpose. Experience at Aberdeen suggests, however, that with strips of $\frac{1}{8}$ in. thickness, reasonable results can be obtained in 3 hours at 145 F, after an initial 3 hours in the first three stages of the four-stage system. Final drying is, of course, prolonged if the material entering the deep tray is initially of higher moisture content, but this type of equipment will satisfactorily handle pieces of root vegetable with water ratios up to about 0·2; at higher water contents shrinkage of the mass of material in the tray, and a tendency for wet patches to remain, necessitates periodical raking over of the mass.

Effects of operating variables

The effects of operating variables have not been studied as fully in the four-stage system as in the three-stage, but there is no reason to believe, for example, that the effects of differences in tray load and in piece thickness would be altered. One major difference, however (related to the particular equipment at Aberdeen and not to the four-stage system *per se*), is the ability to use much higher temperatures in the first stage, up to 260 F. Tucker & Bhatia[8] have examined drying rates using various combinations of conditions in the earlier stages of dehydration, and although their experiments were not designed to examine four-stage drying as such, their results may have some relevance in this connection.

In each of their experiments, drying curves were obtained for single batches (about 550 lb.) of scalded potato strips, either $\frac{1}{8} \times \frac{5}{16}$ or $\frac{3}{16} \times \frac{5}{16}$ in. cross-section, subjected to various temperature conditions, ranging from five stages in steps of decreasing temperature, to one stage only at a constant temperature; a typical series of curves is shown in Fig. 8. Conditions in the dryers were, however, not typical of the type of multi-stage drying being considered in this paper. The use of single batches meant that the drying system as a whole was being operated at well below the normal load, and consequently the humidity of the air circulating over the vegetable was substantially less than under normal circumstances. For example, when the system is operating under full load, with dry-bulb temperature in the first stage 230 F, the wet-bulb temperature rises to about 130°F; in the experiments of Tucker & Bhatia, when the dry-bulb was 230°F the wet-bulb was between 115 and 120°F.

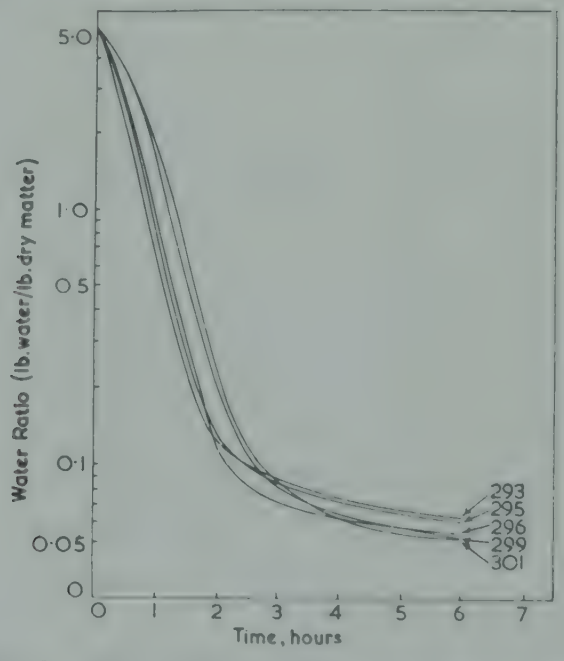

FIG. 8. *Effect of different drying conditions on water ratio of potato strips* $\frac{1}{8} \times \frac{5}{16}$ *in. cross section*

The drying curves show, as might have been expected, that in the initial stages the rate of water loss was greatest at the higher temperatures. Whatever the early temperatures, however, the water ratio curves of the partly dried products approached each other at some time between 2½ and 4 hours after the start of drying; although there were differences in this respect in the various experiments, it did not appear that a higher initial rate of drying led to lower moisture contents at the end of a 6-hour drying period. On the contrary, there was some evidence in one group of experiments that the material dried most quickly in the early stages (initial temperatures 250 F and 230 F), dried more slowly in the later stages, and finished with a slightly higher moisture content than material which had lower initial temperatures (210 and 190°F).

The possibility of inducing 'case hardening' by rapid evaporation in the early stages of drying has frequently been mentioned in the literature. As the potato tissue dries, the outside of each piece forms a closely packed layer of collapsed cells, gelatinized starch and deposited solutes; this condition is presumably accentuated by more rapid drying and is said to lead to slower drying in the later stages. Ede & Hales[1] attempted to induce this condition, but were unable to find any evidence for it, and it has not appeared in the experience of the present writers

at temperatures of 210 F or below. The results of Tucker & Bhatia, however, suggest that an effect of this kind may occur at 230 and 250 F. Certainly the figures suggest that in a cross-flow system there may be no ultimate advantage in raising the initial temperature much above 210 F, unless a final water ratio as high as 0·1 can be tolerated.

Discussion

All the results with the three- and four-stage systems reinforce the common experience of dehydrators, that drying to a water ratio of about 0·15 to 0·10 is relatively rapid and may be accomplished by a wide variety of different conditions with relatively little difference in time, but further drying to moisture levels of about 0·05 is inevitably prolonged. It has been shown that a three-stage system reduced the drying time compared with a particular design of two-stage tunnel, and that a four-stage system had certain advantages over a three-stage system. In practice, the four-stage system has been satisfactory and it seems to be the reasonable limit to which elaboration should be carried, but the results of Tucker & Bhatia's recent experiments again raise the question as to whether the complication and capital outlay of a multi-stage system is, in fact, justifiable.

It has already been seen that parallel-flow tunnel dryers have the disadvantage that air is blown over a series of trolleys so that each succeeding batch of vegetable is affected by those upstream. Further, although tunnels are relatively simple in some respects, the large fans and heaters required, the mechanical pusher gear necessary to move the long line of trolleys, and the brickwork, are costly.

In cross-flow dryers the nature of the airflow minimizes the first drawback (though it does not necessarily entirely eliminate it, since, if the trolleys are in pairs side by side, the upstream member of the pair affects the downstream member). In such systems, it is possible by appropriate control of recirculation and air intake to keep the humidity low at any stage (which is not possible in a tunnel dryer), and initial dry-bulb temperatures as low as 170 or 160°F can be used to bring thin potato strips to almost the same water ratio in 3–4 hours as drying with a series of very much higher temperatures.

One point which should be made here is that if the initial dry-bulb temperature of the air is low, 160–170 F, the corresponding wet-bulb temperature may be only about 90–100°F, which is the optimum temperature for the growth of many types of bacteria. If the material being dried has been steam-scalded after tray spreading, it may be expected to be virtually sterile when drying commences: on the other hand, water-scalded material which has been cooled and spread on trays after scalding may become contaminated during this handling. In such cases serious proliferation *may* occur during the early stages of drying under these conditions: although this has not been found to happen if plant hygiene throughout is really satisfactory, it is a danger that must be taken into consideration. Haines & Elliott[9] consider that drying conditions should be such that the material being dried should reach a temperature of 125 F in the first hour if satisfactory bacteriological control is to be attained.

The quality of the material produced by the various temperature combinations has appeared to be the same, unless *visible* heat damage was present. No evidence has been found to indicate that latent browning (heat damage) ever occurred nor, so far, has any difference in culinary quality been detected in potato dried with different initial temperatures. There is a possibility —but no experiments on this aspect have so far been carried out—that high initial dry-bulb temperatures may be aggravating the loss of volatiles during drying; this could be important in carrot and cabbage. Again, there is a possibility (also unexamined) that excessively prolonged drying might lead to some degree of oxidation of certain products.

For drying at single temperature or two temperatures only (say 170 F followed by 145 F dry-bulb), single-cabinet systems (or single cabinets followed by deep-tray or bin dryers) would appear to be suitable. The comparison then lies between this type of equipment and the four-stage system described above. Assuming that in each system the drying times would be similar, the same amount of cabinet space would be required, the same number of fans and the same number of heaters, to handle the same amount of vegetable. In the cabinet system, assuming that low initial temperatures were to be used, smaller heaters or steam at lower pressure could be employed, and this seems to be the only advantage. Thermal efficiency is at a disadvantage; while in the earlier stages of drying the warm air leaving the cabinets will have a heavy load of moisture, in the later stages it will be leaving far short of saturation and capable of carrying

out considerably more evaporation; in the four-stage system the heat in the warm air discharged from the later stages is usefully employed in the earlier stages. At the time of writing, experiments are in progress to assess the extent of the differences between the systems in this respect, but the theoretical basis of the superiority of the multi-stage counterflow system is clear.

When these various factors are taken into consideration, therefore, it does seem that a multi-stage system, employing countercurrent air flow with interstage reheating and combined with bin or deep-tray finishing, is probably the most economical and generally satisfactory system for overdraught dehydration on a commercial scale. The optimum conditions for the early stages of drying cannot yet be stated, but any great acceleration in the initial rates of water removal is unlikely to be of much advantage.

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Discussion

Mr. A. J. Scott: Mr. Gooding's paper raises a number of points which affect the design of practical dehydration equipment, and are therefore worthy of consideration in some detail.

Many dryer calculations are based on the more or less well-founded assumption that the material to be dried possesses a well-defined critical moisture content, above which constant-rate drying takes place, and below which there may be one or more falling-rate periods of drying depending on the final moisture content of the dried material. The constant-rate period, as has been pointed out, is characterized by the raising of the material temperature to the wet-bulb temperature of the drying air, and this effect has been noted in commercial drying equipment in support of the experimental work cited by Mr. Gooding, the critical moisture content for peas, for example, being of the order of 2·8–3·2 lb. of moisture/lb. of dry material, as far as could be determined from the necessarily rather rough data obtained. It may of course be possible to demonstrate that constant-rate drying is due entirely to the excess free moisture associated with the feed material on account of previous washing or blanching operations, but there is no doubt that this must also be taken into account when sizing a dryer for a particular duty.

Although in theory it is the wet-bulb temperature of the drying air that is attained during constant-rate drying, practically the drying surface is somewhat hotter in most cases due to radiation and conduction of heat from surrounding metal surfaces.

The measurement of constant-rate drying periods may be affected in beds of material of some depth by the gravitational effect on free moisture. Thus it is possible that the upper surface of a bed can dry off and its temperature start to rise before the critical moisture content of the bed as a whole has been attained, so that practical drying tests on beds of significant depth may not yield information directly comparable with that from experiments on, say, single strips of material. This is equivalent to saying that there will be moisture gradients within the bed as a whole as well as in the individual particles that go to make up the bed, and these may be of importance, not only as regards estimation of critical points but also with regard to measurement of bed temperature. It should also be noted that temperature measurements made with thermocouples are also liable to error due to conduction of heat along the thermocouple wires, an effect noted by McEwen in experiments relating to the drying of wheat grain and mentioned by Rolfe in experiments on A.F.D. drying of meat. It is possible that an effect such as this is responsible for the apparent lack of constant-rate drying in vegetable dehydration as reported by Ede.

Since during evaporation heat transfer is involved as well as mass transfer, two equivalent expressions involving the relevant conditions can be used to predict the constant, drying rate.

Thus,

$$\left(\frac{dW}{d\theta}\right)_c = \frac{h\Delta t_m}{\lambda L} = \frac{kg\Delta p_m}{L}$$

where $\left(\frac{dW}{d\theta}\right)_c$ = drying rate, lb./h. lb. dry material

h = heat transfer coefficient, B.Th.U./h. sq. ft. °F

Δt_m = mean temperature difference between air and material (°F)

L = bed loading, lb. dry material/sq. ft.

For small surfaces, Δt_m will be sensibly equal to the wet-bulb depression of the drying air, but for large surfaces alternative means must be used to evaluate Δt_m since the air will cool down appreciably in its passage over the surface. A method involving the concept of transfer units is available to modify Δt_m to the required value, leading to a result similar to that demonstrated by Powell but having the advantage of presenting a rather clearer picture of what is happening.

The constant-drying rate is thus very definitely a function of the wet-bulb depression, and for small surfaces will be more or less directly proportional to it.

The heat transfer coefficient h is expressed as a function of the air velocity or mass flow rate,

$$h = k_1 V^{0.8}$$
$$= k_2 G^{0.8}$$

where k_1 and k_2 are constants,

V = air velocity, ft./sec.

G = air mass velocity, lb./h. sq. ft. cross-section,

so that the over-all drying rate expressed in this way corresponds closely to that given by Powell with the exception of a shape factor, which, however, is not of importance in most industrial applications.

The falling-rate period is very often characterized by an expression of the form

$$\left(\frac{dW}{d\theta}\right)_f = A(W-B)$$

where W represents the dry-basis moisture content at time θ and A and B are constants. Since at the critical moisture content W_c, the constant- and falling-rate periods coincide, the constant A can be evaluated.

Thus, $$\left(\frac{dW}{d\theta}\right)_f = \left(\frac{dW}{d\theta}\right)_c = A(W_c - B)$$

$$\text{or } A = \left(\frac{dW}{d\theta}\right)_c \Big/ (W_c - B)$$

$$\text{Therefore } \left(\frac{dW}{d\theta}\right)_f = \left(\frac{dW}{d\theta}\right)_c \cdot \frac{W - B}{W_c - B} = K\frac{(W - B)}{(W_c - B)}$$

where K represents the constant drying rate.

In view of this it is difficult to explain the effect demonstrated in the experiments of Tucker & Bhatia, where high air temperatures led to an initially high drying rate, as expected, followed by a tailing-off to a rate lower than that produced by lower air temperatures. The above expression indicates that a higher constant rate should be accompanied by a higher falling rate, at least down to fairly low moisture contents. No doubt the method of conducting the experiments in series dryers would tend to modify the predicted results to some extent, but it seems far more likely that 'case-hardening' is responsible for the anomaly.

Mr. Gooding: I am grateful to Mr. Scott for his useful comments, and I do agree that, at any rate where scalded vegetables are concerned, account must be taken of a constant-rate period in the earlier stages of drying, and that the constant-drying rate will be a function of the wet-bulb depression, which in its turn, of course, depends on the design of the dryer in use (i.e., on air flow and tray loading).

With regard to the falling-rate period however, it is true that a higher constant rate produced by higher drying temperatures would be followed by a higher falling rate, provided the higher temperatures were maintained. In the experiments of Tucker & Bhatia, however, after the initial 30 minutes at 250°F or 230°F or 210°F, the dry-bulb temperature was reduced to 185°F or 190°F. The constant-rate period occupied a portion of the first half-hour, but the falling-rate period would have started before the temperature was lowered. We have no means of saying when this occurred, but what we do know is that, at the time the temperature was reduced, the water ratios of the product were very different, as shown in the table below for potato strips $\frac{3}{16}$ in. thick.

Dry-bulb temperature for first ½-hour, °F	Water ratio of vegetable (lb. of water per lb. of dry matter) after ½-h. drying
260	1·82
250	1·84
230	2·18
210	2·39
190	2·92
160	3·13

At the time when the temperature is reduced, then, material which has been subjected to higher initial temperatures has substantially lower moisture contents than material subjected to lower initial temperatures—in other words, it has already progressed further along the falling-rate period, so we would expect the rate of drying at any particular time from the start of drying to be less. This, of course, is what did appear in practice.

I still do not know to what extent case-hardening, if it has really appeared at all in these experiments, affects the rate of drying. We have done a considerable number of experiments since this paper was written and we now doubt whether the differences in final moisture content found in the dried products in Tucker & Bhatia's experiments are significant.

With regard to Mr. Scott's last point about series dryers, the experiments of Tucker & Bhatia were, in fact, carried out with only a single pair of trolleys in the dryer; one cabinet was used for the initial high-temperature stage, and a second cabinet for the remaining temperature stages.

Mr. A. J. Ede: I think it will be accepted that anyone encountering vegetable dehydration for the first time is apt to be dismayed at the labour involved in loading and unloading trays at a mere pound or so to the square foot. Nevertheless, the practice continues; the main reason is to be found in the nature of the wet material: freshly scalded shreds are soft, fragile and sticky, and any attempt to dry them in bulk encounters severe difficulties.

It is a fact, however, that individual shreds, if exposed to a rapid current of reasonably hot air, quickly develop a skin which renders them free from stickiness and much more robust, in fact much more manageable altogether.

I have long speculated on the possibility of shaking out the shreds from the scalder into a really thin layer on a rapidly moving conveyor belt, and there exposing them to hot air in order to achieve this preliminary drying: the time need not be very long, and so the belt need not be of unmanageable size. It should then be possible to transfer the strips to a normal belt dryer, using a much heavier loading—perhaps several inches thick—without encountering the penalties which follow when the same procedure is attempted with wet shreds.

I wonder if Mr. Gooding has ever attempted anything on these lines?

Mr. Tucker: We have carried out some experiments with conveyor-belt dryers, but have not investigated the effect he mentions. With leafy materials such as cabbage, the tendency of the pieces to mat together results from their limpness as much as from their stickiness and, in our experience, shreds of scalded cabbage do not separate freely until about half the original water content has been removed. Strips of potato, carrot, and other root vegetables are much easier to handle, and these could probably be treated as Mr. Ede suggests.